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FINAL REPORT

APPLICABILITY OF ORGANIC SOLIDS TO THE DEVELOPMENT OF NEW TECHNIQUES FOR REMOVING OXIDES OF SULFUR FROM FLUE GASES

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15 APRIL 1970

PREPARED FOR:

THE AIR POLLUTION CONTROL OFFICE
UNDER CONTRACT NO. PH22-68-46

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FINAL REPORT

APPLICABILITY OF ORGANIC SOLIDS TO THE DEVELOPMENT OF NEW TECHNIQUES FOR REMOVING OXIDES OF SULFUR FROM FLUE GASES

by

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Prepared for:

The Air Pollution Control Office

Under Contract No. PH 22-68-46

15 April 1970

Approved: E. A. Burns
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TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

FOREWORD

This document constitutes the final report for the work accomplished between 24 June 68 and 15 April 70 by TRW Systems for the Air Pollution Control Office of the Environmental Protection Agency under contract PH 22-68-46, entitled "Applicability of Organic Solids to the Development of New Techniques for Removing Oxides of Sulfur from Flue Gases".

This work was conducted under the technical direction of Mr. E. D. Margolin of APCO, Durham, North Carolina. The project was performed within the Applied Chemistry and Chemical Engineering Departments of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division. Dr. E. A. Burns, Manager of the Applied Chemistry Department provided overall program supervision and Dr. R. A. Meyers was Program Manager. Major technical contributions were provided by J. L. Lewis, J. S. Land, C. C. Shih, M. Gardner and A. Grunt.

INTRODUCTION AND SUMMARY

This is the final report on the Area Survey Program for Applicability of Organic Solids to the Development of New Techniques for the Removal of Oxides of Sulfur from Flue Gases (PH 22-68-46) performed by TRW Systems for the National Center for Air Pollution Control (later, the Air Pollution Control Office). The project was performed in three phases during the period from 24 June 68 through 15 April 70. Phase I identified a number of organic solids as having promise for the removal of sulfur dioxide from flue gases. Phase II provided laboratory data on ability of the selected organic solids to sorb sulfur dioxide under simulated stack conditions, and identified cellulosics as the most promising candidate. Phase III assessed the economic potential of cellulosics for removal of sulfur dioxide from flue gases. The report shows

As a result of work performed in Phases I and II of this study, it was shown that, among organic solid sorbents, the most promising class for removal of SO_2 from flue gases is cellulose containing materials such as wood, cotton, and newsprint. In particular, it was found that newsprint regenerably sorbs sulfur dioxide from synthetic flue gas streams at operating temperatures.

Phase III provides preliminary engineering designs and estimates of investment and operating costs for control of four sulfur dioxide contamination sources as requested by the Air Pollution Control Office and shown below: are presented.

Description	Flue Gas Rate MMSCFM	Inlet SO_2 Conc. VPPM	Outlet SO_2 Conc. VPPM
Large New Power Plant	2.5	3×10^3	150
Large Existing Power Plant	2.5	3×10^3	150
Small Existing Power Plant	.5	3×10^3	300
New Smelter	.02	5×10^4	5×10^3

from p. iii

The process designed for utilizing cellulosics would employ a moving-bed of shredded paper as a sorbent of sulfur dioxide from flue gas streams. The sulfur dioxide is subsequently removed from the paper by thermal desorption for use as a feed stream in sulfuric acid manufacture. The economic evaluation of the sulfur dioxide removal and recovery process as applied to the four specified cases led to the conclusion that the process could be attractive compared with other processes for removing sulfur dioxide from flue gases, provided that the newsprint could undergo a large number of regenerations without losing sorptive capacity or decomposing. A brief summary of process economics (utilizing optimistic process assumptions) is presented below:

Description	Capital Cost ($000)	Operating Cost ($/Hr)	($/Ton Coal)
Large New Power Plant Case	12.8	147	0.31
Large Existing Power Plant Case	13.7-17.6	168-257	0.35-0.54
Small Existing Power Plant Case	3.7-4.2	77-81	0.77-0.89
New Smelter Case	0.4	3.80	

The final report, which is a compendium of three program reports, is organized into three divisions:

- Division I, which presents Phase I activities for literature search, selection of candidate sorbents and preliminary engineering analysis,
- Division II, which describes Phase II activities for laboratory screening and detailed accumulation of data, and
- Division III, which presents preliminary process designs and cost estimates.

Each division is organized with an internal table of contents and numbering system for sections, tables, figures, equations and references.

DIVISION I

PHASE I

Literature Search and Preliminary Chemical Systems Analysis

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1.0 INTRODUCTION AND SUMMARY

This report division presents the Phase I activities for literature search and preliminary engineering analysis. This work had the following objectives:

- To perform a detailed library search and selection of most promising organic solids for removing sulfur dioxide from flue gas, and
- To perform a preliminary chemical systems analysis for candidate SO_2 removal materials.

As a result of a detailed literature search and conceptual analysis, a number of organic solids were identified as having capacity for the binding of sulfur dioxide. A principal accomplishment of this task was the identification of a number of waste materials which have high potential for removal of SO_2 from flue gases. Organic materials were selected on the basis of:

- Known ability to take up sulfur dioxide,
- Price and availability,
- Thermal stability,
- Regenerability, and
- Mechanical properties.

Five organic materials were identified which offered promise for removing sulfur dioxide from flue gases:

- Cellulosics,
- Nigrosin,
- Poly(N-vinylcarbazole),
- Pyrolyzed poly(vinylchloride), and
- Pyrolyzed poly(acrylonitrile).

The specific cellulosics selected were: waste newsprint, sawdust and cotton.

The results of the preliminary chemical systems analysis indicated that organic solid sulfur dioxide recovery from flue gases may be, in general, economically feasibile where certain criteria are met. The preliminary chemical systems analysis was keyed to thermal regeneration of the organic solids; however, in the case of cellulosic materials, chemical reaction and conversion of the products to useful commodities may also be a feasible process. However, as so little is known as to the parameters involved in these conversion processes at the present time, a consideration of this type of regeneration was not included in the preliminary chemical systems analysis.

2.0 LITERATURE SEARCH
ORGANIC SOLIDS FOR SULFUR DIOXIDE REMOVAL FROM FLUE GASES

A comprehensive literature search through Chemical Abstracts subject heading for sulfur dioxide was completed from the year 1907 to the present. All pertinent sub-categories of the heading sulfur dioxide were searched in detail, e.g., reaction of, reaction with, absorption, etc., with special reference to reaction with organic solids. Thirty-three references were found which dealt with the interaction of sulfur dioxide or nitrogen oxides with organic solids. These are listed in Section 5.0 along with a general bibliography of all references obtained during the literature search. Of the references on organic solids, only those concerned with the use of ion exchange resins addressed themselves to the specific problem of removing sulfur dioxide from gas mixtures and none of the ion exchange papers discussed the temperature region applicable to flue gas stacks (these being 215-300°F after the preheater region of the flue gas stack and approximately 600-650°F before the preheater region). This lack of high temperature testing of the ion-exchange resins is probably due to the fact that most of the resins contain either pendent amino groups or single-strand organic backbones which are relatively thermally unstable. Several references provided information showing that cellulosic materials take up appreciable quantities of SO_2 at room temperature. It had originally been hoped that data such as adsorption and desorption rates of sulfur dioxide, activation energies of organic solid-gas reactions, etc., at room temperature, or better flue gas stack temperatures, would be available from the literature. Unfortunately, where references were found to be specific for organic solid-sulfur dioxide interactions, these studies were conducted almost entirely at temperatures equal to or well below room temperature.

The results of the literature search and conceptual studies are presented below in three sections:

- Organic solids which interact with sulfur dioxide,
- Criteria for selection of most promising organic solids, and
- Most promising organic solids for removal of sulfur dioxide from flue gases.

2.1 ORGANIC SOLIDS WHICH INTERACT WITH SULFUR DIOXIDE

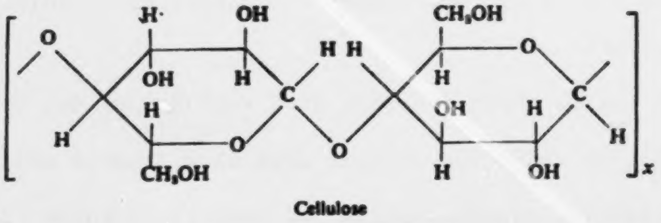
Approximately 32 references were found which described the interaction of sulfur dioxide with organic solids. The information contained in these references is summarized in Table I which contains a classification of organic solid-SO_2 interactions, together with information generated at TRW Systems prior to the start of this contract. In this section, each organic solid will be discussed individually in the following organic solid subdivisions:

- Polymers - cellulosics,
- Polymers - ion exchange,
- Polymers - miscellaneous,
- Homocyclic aromatics and derivatives,
- Heterocyclic aromatics and derivatives,
- Telomeric dyes and dye bases, and
- Organo-metallics

2.1.1 Polymers - Cellulosics

Cellulose is obtained from and makes up a large part of the structure of wood, cotton, ceral, straw, hemp and jute among others. Paper is a major commercial cellulosic product which consists largely of cellulose that also includes fillers, binders, and pigments. The 1966 total U. S. production of paper products was 46.5 million tons which included the following major forms: paper, paperboard and construction paper, while the total newsprint consumption in the U.S. was 9.1 million tons of which 6.7 million tons were imported from Canada.

Cellulose is a ladder polymer



Cellulose

TABLE I

CLASSIFICATION OF ORGANIC SOLID - SO_2 INTERACTIONS

Organic Solid Type	Organic Solid	Interactions	References
Polymer	Cellulosics (paper, wood cotton), etc.	Insertion, change-transfer	2 - 8
	Ion exchange resins (divinylbenzene-methylvinylpyridine copolymer and other amine containing polymers)	Change-transfer, acid-base	9 - 15
	Poly(N-vinylcarbazole)	Change-transfer, acid-base	21
	Pyrolyzed Poly(acrylonitrile)	Change-transfer, acid-base	21
	Conjugated double bond containing resins pyrolyzed poly(vinyl-chloride)	Addition	22
	Linear saturated polymers (Teflon, poly(propylene), poly(vinyl-chloride, etc.)	Absorption-Adsorption	16 - 20
Homocyclic Aromatics and Derivatives	Anthracene	Change-transfer	23 - 24
	Hydroquinone	Inclusion compound	25 - 26
	Coal*	Change-transfer, acid-base	27
Heterocyclic Aromatics and Derivatives	Phenothiazine	Change-transfer, acid-base	28
	Dianin	Inclusion compound	29 - 30
Hydrocarbons and Derivatives	Camphor	Change-transfer	31
	Cyclohexylhydroxylamine	Insertion	32
Telomeric Dyes and Dye Bases	Nigrosin	Change-transfer, acid-base	21
	Copper Phthalocyanine	Change-transfer, acid-base	22
Organo Metallics	Tri-n-dodecyl Aluminum	Insertion	34
	Alkali metal salts of fatty acids Alkali metal salts of benzoic acid	Insertion, acid-base	33

*Coal is a complex mixture of homocyclic and heterocyclic aromatics.

which because of this is highly thermally stable. Cellulose materials generally do not begin rapid thermal decomposition below 500-600°F (1). Hence, cellulose derivatives from a thermal stability standpoint are applicable to flue gas stack region in the area after and possibly before the preheater. Take up of sulfur dioxide and other gases by cellulose has been studied in some detail at or near room temperature. It has been shown that cellulose itself absorbs, in order of decreasing volume: sulfur dioxide, carbon dioxide and oxygen (this is the same order as charcoal) (2). It has also been shown that sulfur dioxide absorption by various cellulose derivatives varies according to the heat pretreatment of the cellulose derivative (3). At room temperature, hydrophilic cotton absorbs 3% by weight sulfur dioxide, filter paper, 3.2% by weight, filter paper heated at 173°C prior to sorption 4.3%, filter paper heated to 320°C takes up 2.98%, hydrophilic cotton heat dried at 150°C takes up 13.88% and nitro cellulose takes up 16.89%. In another paper it is stated that wood takes up more sulfur dioxide than does cotton (4), and that carbon dioxide is not appreciably absorbed by wood. Galzova shows that sulfur dioxide is taken up by cotton during a drying process (5), while Hudson shows that printing paper takes up very small amounts of sulfur dioxide from the atmosphere under ambient conditions (6 - 8).

It is clear from these results that sulfur dioxide is taken up in appreciable quantities, as much as 17% by weight at room temperature by cellulosic materials. This uptake probably occurs by a combination of charge-transfer interactions and insertion reactions.

CHARGE TRANSFER

$$\text{CELLULOSE} + n\,\text{SO}_2 \rightleftharpoons \text{CELLULOSE}\cdot(\text{SO}_2)_n$$

$$K_{\text{equil}} = \frac{\left[\text{CELLULOSE}\cdot(\text{SO}_2)_n\right]^n}{\left[\text{CELLULOSE}\right]\left[\text{SO}_2\right]^n} \qquad (1)$$

CHEMICAL REACTION

$$\text{CELLULOSE}\!-\!(\text{OH})_n + n\text{SO}_2 \rightleftharpoons \text{CELLULOSE}\!-\!(\text{OSO}_2\text{H})_n$$

$$K_{\text{equil}} = \frac{\left[\text{CELLULOSE}\!-\!(\text{OSO}_2\text{H})_n\right]^n}{\left[\text{CELLULOSE}\!-\!(\text{OH})_n\right]\ \left[\text{SO}_2\right]^n} \qquad (2)$$

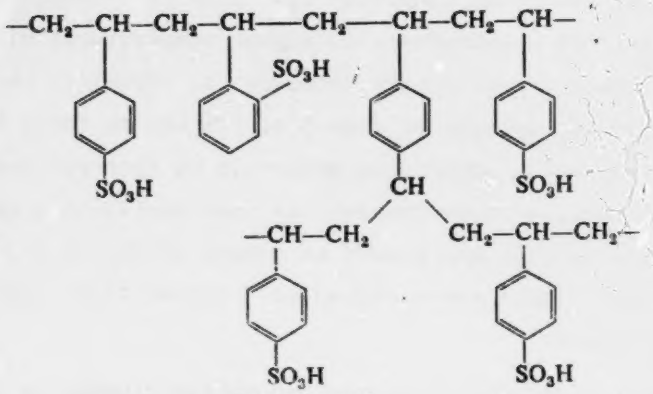
Change transfer interactions (Equation 1) are generally exothermic processes and the equilibrium constants decreases as temperature increases, as does ordinary sorption. Thus the higher temperatures encountered in flue gases will tend to decrease strongly this type of sulfur dioxide uptake. However, it is hoped that the major part of the SO_2 uptake is due to the second reaction, that of insertion (Equation 2). This is a chemical reaction which will very likely be endothermic and higher temperatures will increase the equilibrium constant rather than decrease it. Thus, it may be anticipated that sulfur dioxide uptakes of from 5 to 10% may be found for at least some of the cellulosic containing materials at flue gas temperatures of 215-300°F. Indeed, a rough feasibility test utilizing a gas stream which was 30% SO_2 w/w in nitrogen showed an uptake of SO_2 at 215°F by ground waste newsprint. There are a number of "regeneration" possibilities for cellulose materials:

- Regeneration of cellulose and sulfur dioxide by use of heat, inert gas, vacuum, solvent extraction (water, amines, etc.)
- Hydrolysis of cellulose to glucose by action of bound sulfur dioxide (from flue gas) together with water.

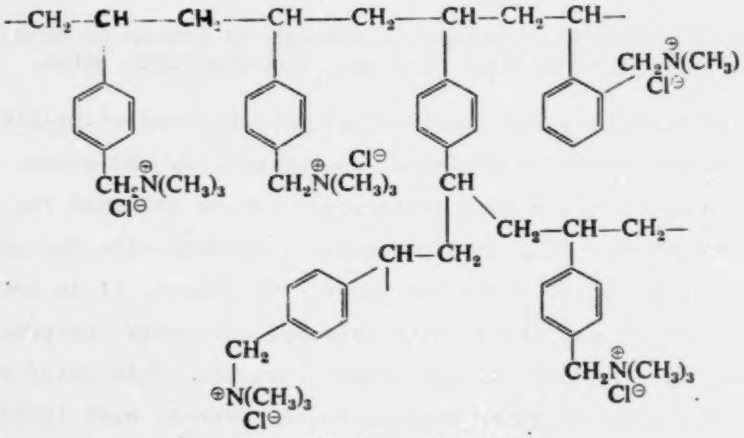
It is very difficult to set absolute prices for these materials as the prices are highly variable depending on the quality and grade. It has, however, been ascertained that waste paper can be obtained for roughly 0.3 cents per pound. This compares quite favorably with the price of activated charcoal of 10 cents per pound. Of course, it is readily apparent that all of the cellulosic materials are extremely inexpensive relative to pure chemical compounds or activated charcoal. This brief study, which will survey a number of other organic solid classes, must limit itself to a few cellulosics, specifically: sawdust, (approximately 50% cellulose), cotton, (almost 100% cellulose), and waste paper specifically newsprint (roughly 75% cellulose).

2.1.2 Polymers - Ion Exchange

Ion exchange resins both cation and anion types have been studied in some detail with regard to their ability to sorb sulfur dioxide. The structure of typical cation and anion exchange resins are shown in the figure below.



Cation exchange resin



Anion exchange resin

Figure 1. Structure of Ion Exchange Resins

As much as 0.25 gram of sulfur dioxide per gram of ion exchange resin has been reported to be obtained at room temperature for typical ion exchange resins at equilibrium (9) and comparisons have been made between ion-exchange resins and typical inorganic sorbents such as activated charcoal, molecular sieve and silica gel (9-13) in which the ion exchange resins were shown to be satisfactory for low temperature sorption but not equivalent to the inorganics. Clearly, the linear structure of ion exchange resins coupled with the thermal instability of the pendent acid and base groups limits their use in actual flue gas environments. It has been shown that ion-exchange resins based on copolymers of 2-methyl-5-vinylpyridine and p-divinylbenzene sorb sulfur dioxide from moving gas streams at low temperatures (60°C), and these sorbents may be regenerated by combination of hot air and ammonia, or sulfur dioxide may be oxidized to sulfur trioxide on the catalytic surface formed by the ion exchange resin, again at relatively low temperatures (14, 15).

2.1.3 Polymers - Miscellaneous

Several researchers have studied the interactions of sulfur dioxide with various construction materials including plastics at ambient levels (1 to 100 pphm. vol.) and at ambient temperatures (20-35°C) (16-19). These workers have shown that materials, such as stainless steel, Teflon, Tygon, glass, poly(propylene), poly(vinylchloride), etc., sorb small amounts of sulfur dioxide from the atmosphere. Further, it has been shown that sulfur dioxide, nitrogen oxide, etc., catalyze thermal decomposition of poly(tetrafluoroethylene) at 450-500°C (20). However, the nature of these materials and the low degree of sulfur dioxide sorption coupled with relative thermal instability indicates that they are of little interest with regard to the problem of removing sulfur dioxide from flue gases.

Recent studies at TRW Systems have shown that TRW processable polyimides ($10-30/lb for prepolymer), poly(N-vinylcarbazole) ($5/lb), and 8-hydroxyquinoline-formaldehyde polymer (unavailable commercially) remove sulfur dioxide from moving gas streams at 460°F (on fire brick) (21), and these organic solids are thermally stable according to thermogravimetric analysis in air at temperatures encountered in flue gas stacks. However, the high price of the polyimide and relative unavailability of the formaldehyde polymer limit their potential. The change-transfer interaction of N-vinylcarbazole with SO_2 is shown in Figure 2.

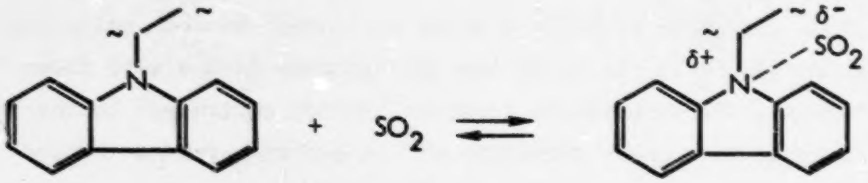


Figure 2. Change-Transfer/Acid-Base Interaction of N-vinylcarbazole with SO_2

In addition, subsequent experimental evaluation at TRW Systems has shown that pyrolyzed poly(acrylonitrile) ($0.60/lb for polyacrylonitrile) and pyrolyzed poly(vinylchloride) ($0.15/lb for poly(vinylchloride), however, as a possible waste product it could cost only the price of transportation), also takes up sulfur dioxide from moving gas streams (22) probably via change-transfer or acid-base (Figure 3) and addition reactions (Figure 4) respectively.

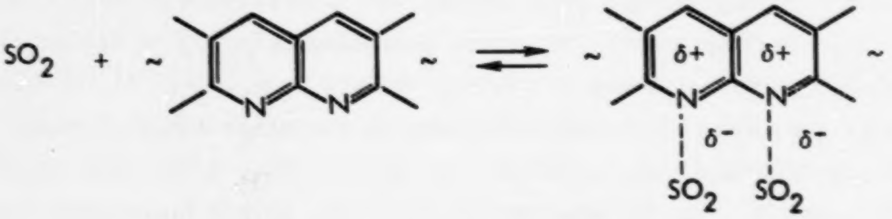


Figure 3. Change-Transfer/Acid-Base Interaction of Pyrolyzed Poly(acrylonitrile) with SO_2

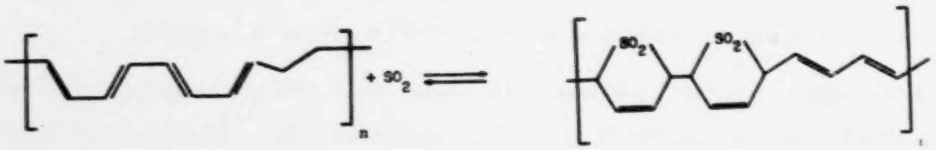


Figure 4. Addition Reaction of Pyrolyzed Poly(vinylchloride) with SO_2

2.1.4 Homocyclic Aromatics and Derivatives

Anthracene has been shown to sorb sulfur dioxide, nitrogen dioxide and oxygen all of which produce a marked increase in the surface photoconductivity of anthracene crystals (23, 24). Hydroquinone takes up (by inclusion compound formation) sulfur dioxide, nitrogen oxide, carbon monoxide and carbon dioxide gases at room temperature and reverts to hydroquinone and gas at approximately 250°F (25, 26), and coal, a complex combination of homocyclic and heterocyclic aromatics has been shown to take up sulfur dioxide at about 300°C with conversion of some of the sulfur dioxide and chemical alteration of the coal (27).

2.1.5 Heterocyclic Aromatics and Derivatives

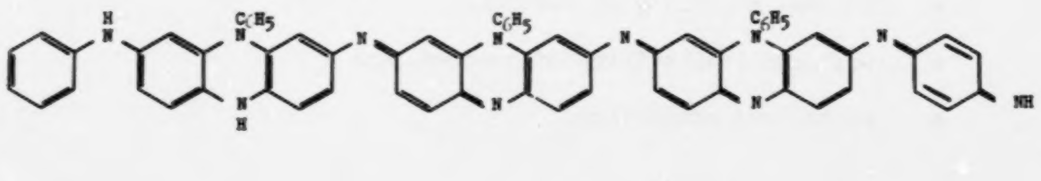
Phenothiazine forms an equimolar complex with sulfur dioxide in solution which is regenerable in the solid state by evaporation of sulfur dioxide at room temperature under vacuum (28). Dianin,(p-3,4-dihydro-2,2,4-trimethyl-2-H-1-benzopyran-4-yl) phenol, forms inclusion compounds with sulfur dioxide and other flue gas components. The molecular structure of these inclusion compounds or clathrates have been studied in detail by infrared spectroscopy (29, 30).

2.1.6 Hydrocarbons and Derivatives

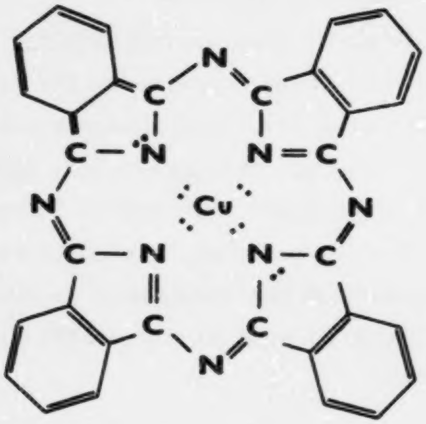
Camphor forms 1:1 and 1:2 complexes with sulfur dioxide above -16°C. Equilibrium pressures of the camphor-sulfur dioxide system were measured at several temperatures ranging from -38° to $+38^{\circ}$C (31). Cyclohexylhydroxylamine reacts with sulfur dioxide at -10°C to give cyclohexylsulfamic acid (32).

2.1.7 Telomeric Dyes and Dye Bases

Recent studies at TRW Systems have shown that nigrosin ($2.75/lb), an aniline black derivative (21),



and copper phthalocyanine (22),



remove sulfur dioxide from moving gas streams at 460°F. No mention of either of these dyes or indeed of any dyes was found in the literature with regard to take up of sulfur dioxide. It appears that these dyes, which are highly thermally stable, take up sulfur dioxide by charge-transfer or possibly acid-base interactions.

2.1.8 Organo Metallics

Alkali metal salts of benzoic and fatty acids add gaseous sulfur dioxide at a slow rate in the ratio of approximately 1 mole of sulfur dioxide to 1 mole of compound at temperatures above $0^{\circ}C$ (33). Tri-n-dodecyl aluminum reacts with 3 moles of sulfur dioxide per mole of compound yielding aluminum trisulfonates which can later be hydrolyzed to sulfamic acids (34).

2.2 CRITERIA FOR SELECTION OF MOST PROMISING ORGANIC SOLIDS

At this point in the program, the basic criteria which may be used for the selection of organic solids for Phase II evaluation for the removal of sulfur dioxide from flue gas emission stacks,are the following:

- Ability of sorbent to remove SO_2 from flue gas at operating temperatures at a high rate,
- Thermal stability of sorbent,
- Cost and availability of sorbent, and
- Mechanical properties.

It is clear that the primary requirement of the organic solid for the removal of sulfur dioxide from flue gases is ability to remove sulfur dioxide selectively from moving gas mixtures at the flue gas operating temperatures and at a relatively high rate (typical contact times are in the order of a second). The sorbent must be thermally stable at the temperature of sulfur dioxide uptake (215°F minimum after the preheater region) for at least several minutes. If the sorbent is to be regenerated thermally, it must be stable at even higher temperatures (approximately 600°F) for a period of minutes. The organic solid must be capable of being regenerated or converted to useful products. Regenerability modes could include heat, inert gas, vacuum, solvent extraction, catalytic oxidation, or conversion of the reaction product to a useful commodity chemical. The availability of inexpensive organic solids in large quantities and without any laborious modifications is of major importance. Finally, the mechanical properties of organic solid must be such that the solid is amenable to use in a sorption configuration. That is, the organic solid must be either reasonably porous and finely divided itself or capable of being coated onto a high surface area substrate such as fire brick or activated charcoal.

2.3 MOST PROMISING ORGANIC SOLIDS FOR REMOVAL OF SULFUR DIOXIDE FROM FLUE GASES

Seven specific organic solids were selected for Phase II experimental evaluation on the basis of the criteria stated in Section 2.2. These organic solids are:

- Newsprint (paper),
- Sawdust,
- Cotton,
- Nigrosin,
- Pyrolyzed poly(acryonitrile),
- Pyrolyzed poly(vinylchloride), and
- Poly(N-vinylcarbazole).

The properties of these organic solids as related to the criteria for sulfur dioxide removal are presented in Table II. The organic solids which were selected are all known to take up sulfur dioxide, be thermally stable at flue gas temperatures, to be low in cost, have good mechanical properties and have potential for regenerability. Monomeric organic solids even though known to take up sulfur dioxide were eliminated from this study (e.g., anthracene, phenothiazine, etc.) because of their lack of mechanical properties, that is, they cannot be coated on inert substrates nor can they form mechanically sound sorbent particles. The ion exchange resins were eliminated from this study as they are being evaluated on other NAPCA programs. Polyimides and 8-hydroxyquinoline-formaldehyde polymers were discarded from further consideration because of their very high price.

TABLE II

PROPERTIES OF MOST PROMISING ORGANIC SOLIDS FOR SO_2 REMOVAL

Organic Solid	SO_2 Uptake	Thermal Stability Before Pre-heater 550-650°F (Reg. 2) After Pre-heater 215-300°F (Reg. 1)	Regenerability	Cost and Availability	Mechanical Properties
1. Newsprint (paper 2. Sawdust 3. Cotton	Known to take up SO_2 at R.T. and preliminary results show take up at 215°F by paper	Basic constituent (cellulose) stable region 1	Heat, wash or chemical conversion possible	Waste materials cost of transportation	Can be used as is, ground or shredded, etc.
4. Nigrosin	Known to take up SO_2 at 460°F	Stable regions 1 and 2	Heat or wash possible	\$2.75/lb. in ton quantity	Can be coated
5. Pyrolyzed Poly (acrylonitrile)	Known to take up SO_2 at 460°F	Stable regions 1 and 2	Heat or wash possible	Poly(acrylonitrile) \$0.68/lb in any quantity	Can be coated
6. Pyrolyzed Poly (vinylchloride)	Known to take up SO_2 at 460°F	Stable region 1	Heat or wash possible	Poly(vinylchloride), waste material, cost of transportation	Can be coated
7. Poly(N-vinylcarbazole	Known to take up SO_2 at 460°F	Stable region 1	Heat or wash possible	\$5.00/lb in ton quantity	Can be coated

3.0 PRELIMINARY CHEMICAL SYSTEMS ANALYSIS

This section presents the results of a preliminary chemical systems of processes using organic solids to control sulfur dioxide emissions from flue gases. It was the objective of the analysis to develop preliminary process designs capable of estimating the capital investment and operating costs of systems employing organic solid sorbents and thereby demonstrate the feasibility of these processes.

A large part of the SO_2 pollution problem, 46% of the total in 1966, can be attributed to SO_2 emission from electricity generating power stations. Of the emissions from power stations in 1966, about 91% came from the combustion of coal and about 9% from oil (35). In view of these factors, the preliminary analysis was directed toward the development of a process which could be incorporated into a coal burning power plant. A consideration of the capital expenditure involved in a process capable of handling the large inventory of organic solid sorbent required to control the SO_2 emission from an "average" power plant led to the choice of a fixed-bed mode of operation. A mathematical model, applicable to polymeric organic solid sorbents as well as monomeric sorbents, was formulated to simulate a fixed-bed sorption column, and the model was then translated into a FORTRAN II computer program.

In Section 2.3, candidate organic solids for removal of sulfur dioxide from flue gases were assessed in terms of system criteria and as a result seven organic solids were selected for Phase II evaluation. Of these, the cellulosics appeared to most clearly satisfy the criteria. For example, the 46.5 million tons of paper products produced in the U.S. in 1966 is in line with the estimated 28 million tons of SO_2 per year (approximately 13 million tons of SO_2 per year can be attributed to power station stack gases) emitted to the atmosphere in the U.S. (35). The price of waste paper, roughly 0.3 cents per pound, compares favorably with the price of other sorbent materials(waste paper is approximately 1/30th the price of activated charcoal). In addition, cellulose does not begin rapid thermal decomposition below 500-600°F and, hence, could be used in the gas stack region after the air preheater. Finally, the ability of cellulose to sorb significant amounts of sulfur dioxide has been reported in the literature.

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A process, based on a regenerative fixed-bed SO_2 sorption system with sulfur recovery capability, was specifically designed for a cellulose (paper) sorbent. A computer program, written to evaluate the capital and operating costs of the proposed cellulose - SO_2 sorption process, was combined with the fixed-bed computer program and then utilized to determine the cost sensitivities of the selected independent parameters. The computer program output, which included operating and capital costs, as well as process condition information (sorption batch time, amount of SO_2 sorbed on paper, etc.), is presented in graphical form and can be used to identify operating regions which will result in the maximum profit. The graphs are also an aid in evaluating the effect of a process parameter on the process operating cost.

The results of the preliminary analysis indicates that the proposed cellulose - SO_2 recovery process is economically feasible. In particular, the computer simulation of the proposed process, operating at the selected base case conditions, calculated that a profit of $941,000 would be netted per year (42 cents/ton coal). The total capital requirement would be $2,770,000.

A further consequence of the preliminary chemical system analysis was the development of a computer capability, applicable to a wide range of problems involving SO_2 removal and recovery, which can be adapted to any solid sorbent material operated in batch manner. Only minor revisions in the proposed SO_2 recovery system would be required if organic solids (e.g., nigrosin, pyrolyzed polyacrylonitrile, pyrolyzed polyvinylchloride) were to replace paper as the SO_2 sorbent. Some indication of the effect of sorbent cost on the process operating profit for a SO_2 recovery system equivalent to the proposed system but using a general sorbent material is included in this report.

The results of this study are described under the following five categories below:

- Process Description
- Process Model
- Process Base Conditions
- Results of Parametric Analysis
- Conclusions

The computer program is presented in the Appendix (Section 4.0).

3.1 PROCESS DESCRIPTION

A process for removing and recovering SO_2 from flue gas streams has been developed utilizing the SO_2 sorption capability of cellulose (paper). Figure 5 is the flowsheet of the proposed process as it might be incorporated into a coal-burning power plant (or with minor changes to an oil-burning power plant). There are wide variations between power plants with regard to boiler configuration, the arrangement of heat-recovery equipment, and the temperatures at various positions in the plant, and therefore, the optimum configuration could vary from the one selected here to illustrate the general characteristics of the proposed SO_2 recovery system in a power plant. Although the following process description will apply directly to the paper - SO_2 recovery system of Figure 5, only slight modifications would be required if another organic solid sorbent is used. The major equipment items in the recovery system are three carbon steel sorption columns, a paper shredder, and an induced draft fan. It is believed that three columns may be necessary to assure adequate time to regenerate and replace the paper between each sorption run. Because of the large quantity of sorbent material which must be handled to control the SO_2 emission from a power plant, it was determined that the lowest capital expenditure would result from a fixed-bed mode of operation. If the amount of required sorbent could be significantly reduced below current estimates, a system using fluidized beds or rotating disc contactors may prove economically advantageous. The location of the induced draft fan will be dependent on operating conditions of a particular system and, for this reason, is shown in two possible positions in Figure 5.

The operation of the SO_2 recovery system, as illustred in Figure 5, consists of three phases:

- Sorption of SO_2 by the paper.
- Regeneration of the paper and recovery of the SO_2.
- Replacement of the spent paper.

The high SO_2 content flue gas, after passing through the power plant's dust collector and spark eliminator, enters the fixed-bed sorption column, packed with shredded paper. The SO_2 in the flue gas is sorbed on the paper,

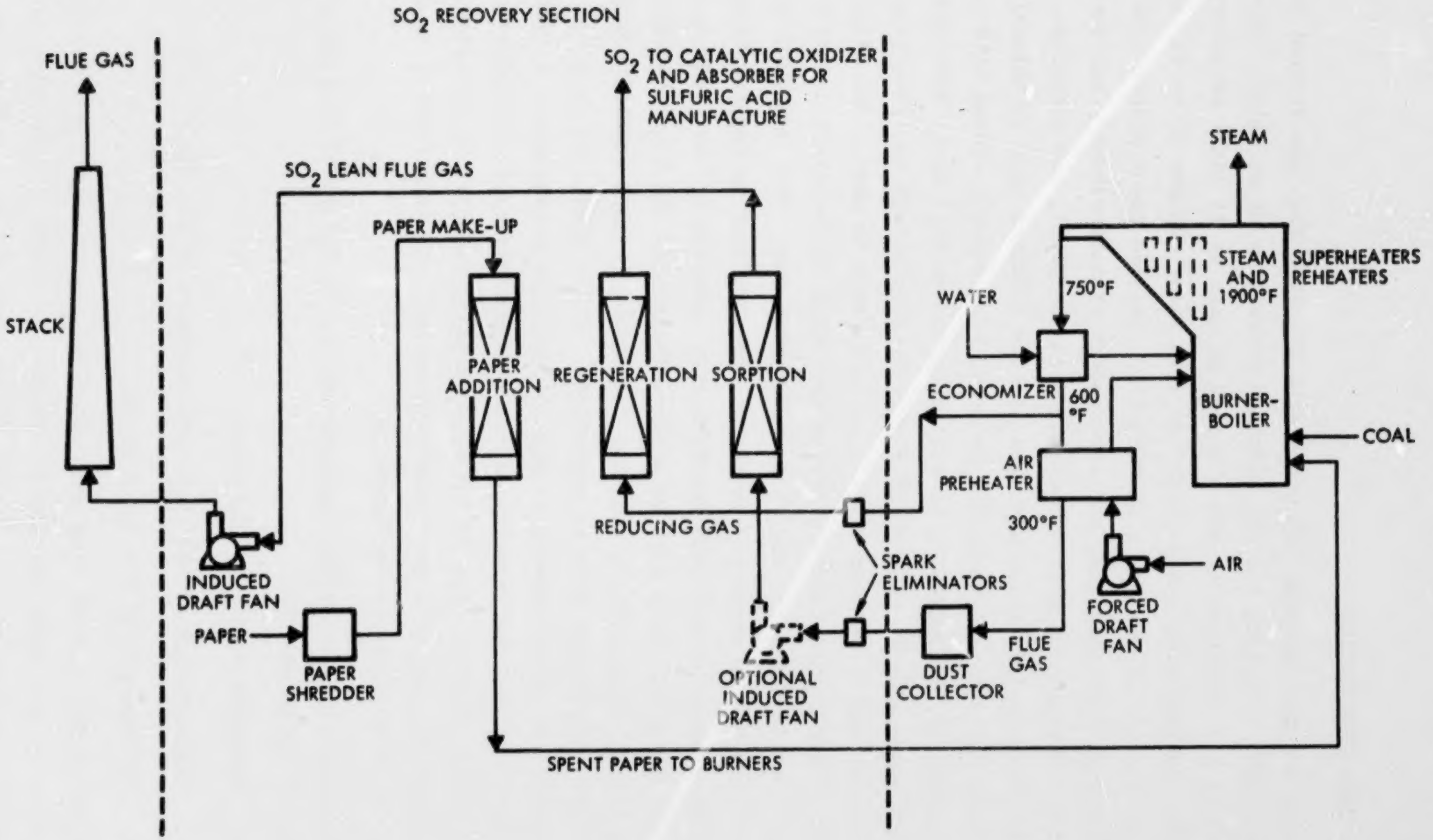
SO$_2$ RECOVERY SECTION
FLUE GAS
STACK
INDUCED DRAFT FAN
SO$_2$ LEAN FLUE GAS
PAPER MAKE-UP
PAPER
PAPER SHREDDER
PAPER ADDITION
SO$_2$ TO CATALYTIC OXIDIZER AND ABSORBER FOR SULFURIC ACID MANUFACTURE
REGENERATION
SORPTION
REDUCING GAS
OPTIONAL INDUCED DRAFT FAN
SPARK ELIMINATORS
SPENT PAPER TO BURNERS
DUST COLLECTOR
FLUE GAS
300°F
AIR PREHEATER
ECONOMIZER
600 °F
WATER
750°F
FORCED DRAFT FAN
AIR
STEAM
STEAM AND 1900°F
SUPERHEATERS REHEATERS
BURNER-BOILER
COAL

Figure 5. Coal Burning Power Plant with SO$_2$ Recovery Capability

and the flue gas, after exiting from the column, is sent to the power plant's stack. The paper also entrains any fly ash that passes through the dust collector. The column operates in this mode until the SO_2 content of the flue gas exiting from this column exceeds the specified pollution limits. When the paper no longer sorbs an adequate amount of SO_2, the flue gas stream is fed to one of the other columns.

After completion of the sorption mode, the paper in the column undergoes regeneration by passing hot flue gas ($600^{\circ}F$) through the column, causing the SO_2 on the paper to desorb. The hot flue gas is drawn from the line separating the economizer (water preheater) and the air preheater. The SO_2 rich gas leaving the column during the regeneration mode is sent to a catalytic oxidizer and converted to SO_3. The SO_3 then undergoes further processing to sulfuric acid.

After regeneration of the paper is completed, some of the paper at the bottom of the column is withdrawn and sent to the burners as fuel. Fresh paper makeup is conveyed from the shredder and added at the top of the column. The column is then ready to begin the sorption mode again.

Stability problems during upsets in the flue gas generating device were not apparent in the proposed process. For example, a temperature runaway in the power plant's boiler would be partially damped in the economizer and air preheater. The flue gas must also pass through spark eliminators which have the capability of spraying water into the gas stream. Even if a fire did occur in a column, the flue gas stream could be diverted to the stack and the fire quickly quenched by a water spray system in the column.

Another problem which could arise is a boiler tube rupture which would send a large amount of steam and water into the system. The water and steam should not cause any serious deterioration of the paper. Along a similar line, an oxygen deficiency in the boiler or a failure of the dust collector, resulting in large amounts of carbon entering the SO_2 recovery system, should not adversely affect the paper and, in fact, the paper would entrain the solid particles in the flue gas.

No major stability problems relating to the SO_2 recovery system itself were uncovered. Paper transfer within the columns will take place by internal vibration. If complete blockage of the paper should occur, manual replacement of the paper would be possible until the problem is rectified. A water spray system will be built into the system as a precaution against fires, and even if a fire does occur in a column, it should not cause extensive damage to the equipment.

Since the spent paper is used as fuel in the boiler, the sorbent does not cause secondary pollution problems. The only secondary pollution should be that encountered in a modern sulfuric acid plant provided the recovered SO_2 is converted to sulfuric acid.

3.2 PROCESS MODEL

3.2.1 Derivation of Mathematical Model

A mathematical model containing technical and economic variables of interest was formulated for the proposed SO_2 recovery process. Since the sorption columns are the major cost items in the process, the technical portion of the model was developed to simulate the unsteady-state operation of a packed bed. The economic portion of the model, utilizing information provided by the technical study, estimates the capital and operating costs of the proposed SO_2 recovery process.

The technical section of the model has the capability of determining the composition of the sorbable component in both the solid and fluid phases as a function of time and position in the column. The description of the technical model deals specifically with an SO_2-paper sorption column, but the approach is of a general form and would apply to the unsteady-state operation of any fluid-solid fixed bed column.

Consider a sorption column in which SO_2 is transferred from the gas phase to the solid phase (in this case paper). With reference to Figure 6, let

G = superficial flue gas flow rate, $\left(\frac{ft^3}{hr - ft^2 \text{ empty column cross section}}\right)$

C_o = SO_2 concentration in feed flue gas (moles SO_2/ft^3)

C_G = SO_2 concentration in flue gas at position Z in the column and at time t, (moles SO_2/ft^3)

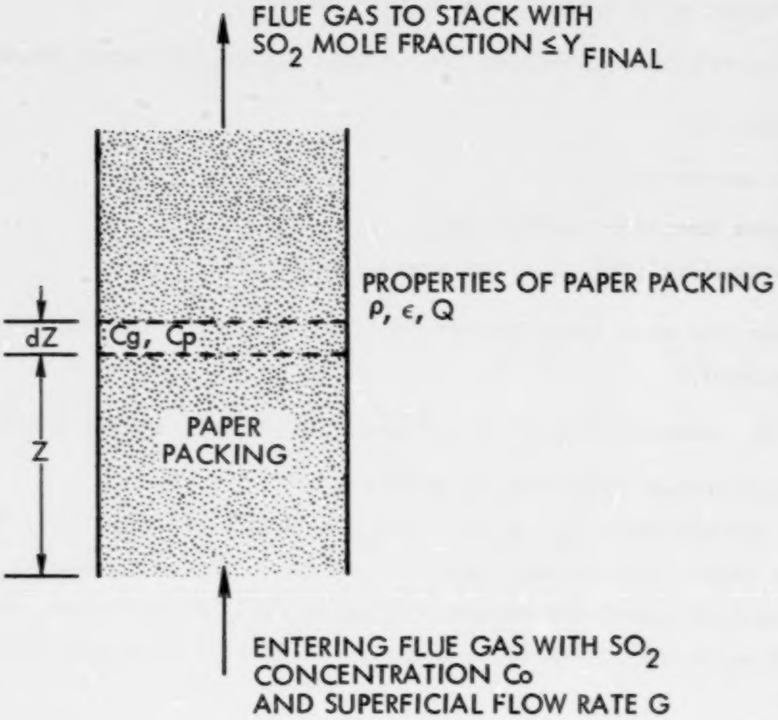
FLUE GAS TO STACK WITH
SO2 MOLE FRACTION ≤ YFINAL
PROPERTIES OF PAPER PACKING
ρ, ε, Q
dZ
Cg, Cp
Z
PAPER PACKING
ENTERING FLUE GAS WITH SO2
CONCENTRATION Co
AND SUPERFICIAL FLOW RATE G

Figure 6. Unsteady-State Operation of a Packed Bed

C_P = SO_2 concentration in the paper at position Z in the column and at time t, (moles SO_2/lb paper).

Q = saturated SO_2 concentration of paper, (moles SO_2/lb paper.

Y = residual SO_2 mole ratio of the flue gas, C_G/C_o.

X = residual SO_2 mole ratio of paper, C_P/Q.

ρ = density of paper, (lbs paper/ft^3 column).

ϵ = void fraction of column (ft^3 actual volume/ft^3 empty column).

t = time, hr.

Z = column height, ft.

k_g = mass transfer coefficient, moles/(hr)(ft^2 transfer area) (moles/ft^3).

a = area for mass transfer per unit volume, (ft^2 transfer area/ft^3 column).

C_i = SO_2 concentration at fluid-solid interface, (moles SO_2/ft^3).

H = equilibrium constant, $C_i = HC_P$.

It will be assumed that C_O, Q, ρ, ϵ, k_g, a, and H are constant, that plug flow exists within the column, and that axial diffusion of SO_2 is negligible. Composition gradients within the paper will be neglected, and mass transferred by diffusion as the result of solid-solid contact will be ignored.

A material balance on the SO_2 contained in an element of unit cross section and of height dZ is

Rate of input: $GC_G = GC_oY$

Rate of output: $G(C_G + \frac{\partial C_G}{\partial Z} dZ) = GC_o(Y + \frac{\partial Y}{\partial Z} dZ)$

Rate of accumulation: $\frac{\partial}{\partial t}[\epsilon C_G + \rho C_p]\, dZ = \frac{\partial}{\partial t}[\epsilon C_o Y + \rho QX]\, dZ$

The SO_2 material balance is then

$$- GC_o \frac{\partial Y}{\partial Z} = \epsilon C_o \frac{\partial Y}{\partial t} + \rho Q \frac{\partial X}{\partial t} \qquad (1)$$

or

$$\frac{\partial Y}{\partial Z} + \frac{\epsilon}{G}\frac{\partial Y}{\partial t} + \frac{\rho Q}{GC_o}\frac{\partial X}{\partial t} = 0 \qquad (2)$$

The term

$- GC_o \frac{\partial Y}{\partial Z}$ accounts for the concentration change of SO_2 caused by flue gas flow

$\epsilon C_o \frac{\partial Y}{\partial t}$ accounts for the SO_2 concentration change in the gas hold-up in the voids

$\rho Q \frac{\partial X}{\partial t}$ accounts for the concentration change of the SO_2 sorbed on the paper

Each term has units of moles/hr-ft^2 empty column cross section.

Similarly, a material balance on the SO_2 in the solid phase is

Rate of input: $k_g a\ (C_G - C_i)\ dZ$

Rate of output: 0

Rate of accumulation: $\frac{\partial}{\partial t}(\rho\ C_p)\ dZ$

the material balance is then

$$k_g a\ (C_G - C_i) = \rho \frac{\partial C_p}{\partial t} \qquad (3)$$

This equation was derived assuming that the diffusion of SO_2 from the bulk of the flue gas to the solid-gas interface is the rate controlling step of the overall reaction of SO_2 and paper.

The assumption is also made that an equilibrium condition exists between the SO_2 at the solid-gas interface and the SO_2 in the paper and that this condition can be expressed by the relationship

$$C_i = HC_p$$

Substituting in (3)

$$k_g a\ (C_G - HC_p) = \rho \frac{\partial C_p}{\partial t} \qquad (4)$$

Rearranging (4) in terms of X and Y

$$\frac{\partial x}{\partial t} = \frac{k_g a\ C_o}{\rho Q}\ Y - \frac{k_g a\ H}{\rho}\ X \qquad (5)$$

Several boundary and initial conditions were added to complete the technical model. If the composition of the entering flue gas is maintained constant

$$Y = 1 \text{ for } Z = 0,\ t \geq 0$$

Also, no change in SO_2 concentration will occur at any point in the packed bed until the entering flue gas has had time to flow down to that point. This condition can be expressed as

$$Y = 0 \text{ for } Z > 0,\ t \geq \frac{\epsilon}{G} Z$$

$$X = 0 \text{ for } Z > 0,\ t \geq \frac{\epsilon}{L} Z$$

where the paper initially has been assumed to have essentially zero SO_2 concentration. By specifying the height of the column (Z_{final}) and the maximum allowable SO_2 mole fraction in the exit flue gas (Y_{final}), the final boundary becomes

$$Y \leq Y_{final} \text{ at } Z = Z_{final},\ \epsilon > 0$$

Equations (2) and (5) along with the above conditions completely define the transient behavior of the fixed-bed sorption column. Solution of this portion of the mathematical model will yield concentration of SO_2 in either the gas or solid phase for any Z or t.

The economic portion of the model estimates the capital and operating costs of the proposed process. The cost-capacity values used to determine the total plant capital cost were obtained by curve fitting data provided in "Cost Engineering in the Process Industries," C. H. Chilton, 1960. All costs were updated to 1968 using the ENR Index and multiplied by their appropriate installation cost factors. For example the equation for determining the sorption column cost is:

$$\text{COLCST} = (2.515 \times 10^{-6} D^4 - 8.99 \times 10^{-4} D^3 + 0.1182 D^2 - 1.079 D + 82.09)\ Z_{final} \times 2.93 \times 2$$

where

COLCST = installed cost of a single tower

D = tower diameter in inches

Z_{final} = tower height in feet

2.93 = updating factor
2.0 = installation factor

The operating costs are calculated assuming that the SO_2 recovery system requires two operators per shift and three shifts per day.

3.2.2 Method of Computer Solution

The mathematical model was translated into a FORTRAN II computer program which was then utilized to determine cost and operational sensitivities of various independent parameters. A description of the method used to obtain a solution to the technical portion of the model, comprised of Equation (3) and (5) along with the corresponding initial and boundary conditions is given below.

Equation (3) can be simplified by the change of variables:

$$S = (\epsilon/G)Z \rightarrow \frac{\partial S}{\partial Z} = \frac{\epsilon}{G}$$

$$\theta = t - (\frac{\epsilon}{G} Z) \rightarrow \frac{\partial \theta}{\partial t} = 1$$

$$\frac{\partial \theta}{\partial Z} = - \frac{\epsilon}{G}$$

then

$$\frac{\partial Y}{\partial Z} = \frac{\partial Y}{\partial S} \frac{\partial S}{\partial Z} + \frac{\partial Y}{\partial \theta} \frac{\partial \theta}{\partial Z}$$

$$= \frac{\partial Y}{\partial S} \frac{\epsilon}{G} - \frac{\partial Y}{\partial \theta} \frac{\epsilon}{G}$$

and

$$\frac{\partial Y}{\partial t} = \frac{\partial Y}{\partial \theta} \frac{\partial \theta}{\partial t} + \frac{\partial Y}{\partial S} \frac{\partial S}{\partial t}$$

$$= \frac{\partial Y}{\partial \theta}$$

Similarly,

$$\frac{\partial x}{\partial t} = \frac{\partial X}{\partial \theta}$$

Substituting the above into Equation (3) and (5) yields

$$\frac{\epsilon}{G} \frac{\partial Y}{\partial S} - \frac{\epsilon}{G} \frac{\partial Y}{\partial \theta} + \frac{\epsilon}{G} \frac{\partial Y}{\partial \theta} + \frac{\rho Q}{GC_o} \frac{\partial X}{\partial \theta} = 0$$

which simplifies to

$$\frac{\partial Y}{\partial S} + \frac{\rho Q}{\epsilon C_o} \frac{\partial X}{\partial \theta} = 0 \qquad (6)$$

and

$$\frac{\partial X}{\partial \theta} = \frac{k_g a C_o}{\rho Q} Y - \frac{k_g a H}{\rho} X \qquad (7)$$

The boundary conditions become

$Y = 1$ at $S = 0$ $\quad \theta \geq 0$

$Y = 0$ at $\theta = 0$ $\quad S > 0$

$Y \leq Y_{final}$ at $S = S_{final}$ $\quad \theta > 0$

$X = 0$ at $\theta = 0$ $\quad S \geq 0$

Equations (6) and (7) were solved on a SDA 940 computer using a finite difference approach known as the "modified Euler's method" or "Henn's first method" (36). The program pertaining to the technical model was written so that the following parameters could be varied:

- cross-sectional area of the column
- height of column
- average column pressure
- average column temperature
- flue gas flow rate at standard conditions (1 atm, 60^oF)
- mole fraction of SO_2 in feed flue gas
- maximum allowable residual SO_2 mole ratio in exit flue gas, Y_{final}
- saturated SO_2 concentration on paper, Q
- weight of paper per unit column volume, ρ
- void fraction of the column, ϵ
- mass transfer coefficient, $k_g a$
- equilibrium constant, H

The technical program outputs the batch time and the total moles of SO_2 which are sorbed on the paper during one batch. The time at which the mole fraction of SO_2 in the exit flue gas exceeds the specified maximum allowable SO_2 mole fraction determines the batch time. Since the moles of SO_2 sorbed on the paper at each sub-interval of height is known, the total moles of SO_2 are calculated by using Simpson's rule to integrate over the height of the column.

The computer program for the economic model allowed the following parameters to be varied:

- paper cost
- SO_2 credit value
- heat credits

The output form the economic portion of the model includes:

- total plant capital cost
- hourly operating cost
- hourly SO_2 credit
- hourly paper credit
- yearly paper usage
- yearly amounts of SO_2 recovered
- total plant yearly cost

3.3 PROCESS BASE CASE CONDITIONS

A study of the proposed SO_2 recovery system was conducted specifically for the case in which cellulose (paper) is the organic solid employed. Each of the technical and economic variables of the computer program was assigned a value, either from known experimental data or from best estimates of parameter, for the base case of operation. References relating to the base conditions are given when possible.

The selected base conditions are:

1. Column diameter = 30 feet
2. Column height, $Z_{final} = 60$ feet
3. Average pressure in column, $P = 14.9$ psi
4. Average temperature in column, $T = 300^{\circ}F$
5. Flue gas flow rate at standard conditions (1 atm, $60^{\circ}F$) = 87.3 million cubic feet per hour[1]
6. Mole fraction of SO_2 in feed flue gas = 0.003 (4)
7. Maximum allowable residual SO_2 mole ratio in exit flue gas, $Y_{final} =$ 0.1 mols SO_2 leaving column per mole SO_2 in feed (3)
8. Saturated SO_2 concentration on paper, $Q = 0.1$ lb SO_2/lb paper (5)

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[1] The flue gas flow rate corresponds to an 800-megawatt power plant burning 280 tons coal/hour (37).

9. Weight of paper per unit column volume, $\rho = 7$ lbs paper/ft^3 column[1]
10. Void fraction of column, $\epsilon = 0.1$ actual volume/column volume[1]
11. Mass transfer coefficient, $k_g a = 20{,}000$ moles/(hr)(ft^3 column)(moles/ft^3)
12. Equilibrium constant, $H = 0.001 \dfrac{\text{moles } SO_2/\text{ft}^3 \text{ gas}}{\text{moles } SO_2/\text{lb paper}}$
13. Cost of paper = 0.3 cents/lb (Reference 5)
14. Credit for SO_2 recovered = 0.5 cents/lb SO_2[2]
15. Heat credit = 50 cents/MM Btu (37, 38).

Two percent of the paper in the column is replaced after each sorption run. The percentage is low, because as paper replacement increases, it becomes exceedingly more difficult to provide an adequate amount of paper to supply the power plant. The heat of combustion attributed to the spent paper is 7560 Btu/lb paper.

The power plant is assumed to burn 280 tons of 4% sulfur coal per hour and to operate at 90% efficiency (330 days/yr). Essentially all of the SO_2 sorbed is removed from the paper during the regeneration step.

The heat required to desorb the SO_2 from the paper was assumed to be of the same order of magnitude as the SO_2 heat of solution in water, and by using this value and a heat cost of 50 cents/MM Btu, the cost of regenerating the paper was estimated at approximately 0.01 cents/lb SO_2. Since the cost of regenerating the paper would have little effect on the SO_2 credit value (0.5 cents/lb SO_2 in the base case), it was assumed negligible.

The SO_2 credit value represents the net worth of the SO_2 as a raw material feed gas. It does not include the cost of converting the SO_2 to a marketable product (i.e., sulfuric acid).

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[1] The density of paper was considered a constant at 70 lbs/ft^3 (39).

[2] The SO_2 credit was evaluated based on a 100% sulfuric acid selling price of \$20/ton (1.5 cents/lb SO_2). It is equated to the market value of 1.5 cents/lb SO_2 less the cost of upgrading the SO_2 to sulfuric acid.

PROCESS COSTS FOR BASE CONDITIONS

The computer simulation of the cellulose-SO_2 recovery system operating at the base conditions described previously produced the following results:

- Batch time = 0.51 hours
- Paper usage = 46,200 tons/year
- SO_2 recovered = 162,600 tons/year
- Total capital cost = $2,770,000
- Operating Profit = $119/hour
  $0.42/ton coal
  $941,000/year

3.4 RESULTS OF PARAMETRIC ANALYSIS

Figures 5 through 29 show the results of the parametric analysis of the paper-SO_2 recovery system conducted by perturbing a selected parameter while maintaining all other variables in the base case conditions. In Figures 7 through 21, the following variables

- Mass transfer coefficient - $k_g a$
- Equilibrium constant - H
- Column diameter
- Column height
- Weight of paper per unit column volume (ρ) - void fraction (ϵ)[1]
- Mole fraction of SO_2 in feed flue gas
- Saturated SO_2 concentration on paper, Q

were plotted as functions of sorption batch time and as functions of operating profits. The operating profit in terms of MM $/yr is calculated assuming that the power plant operates at 90% efficiency (330 days/yr) and the operating profit in $/ton coal assumes that the power plant burns 280 tons coal/hr. The curves are constructed for SO_2 credit values of 1.0 cents/lb and 0.5 cents/lb.

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[1] If the density of paper (DEN) is constant, the weight of paper per unit column volume (ρ) and the column void fraction (ϵ) are related by the expression:

$$DEN = \rho/(1 - \epsilon)$$

Figures 22 and 23 show the effects of column diameter and height on the overall capital costs of the SO_2 recovery system. Figure 24 illustrates the effect of the paper cost on the operating profit of the system. Figures 25 and 26 are graphs of the system's operating profit vs the percentage of paper makeup per sorption cycle, plotted for two SO_2 credit values and two heat credit values. Figure 27 is a plot of the operating profit vs the SO_2 credit value and Figure 28 shows the operating profit as a function of the heat credit value.

Figure 29 is a plot showing the effects of a general sorbent cost in \$/hr on the operating profits of the system. Since the heat credit was assumed zero in the construction of this plot the curves apply to a sorbent which is discarded after releasing the sorbed SO_2.

When applicable, the value of the base case is indicated on the figure. A description of each of the graphs follows.

Figure 7

This plot shows the SO_2 sorption batch time in hours vs the mass transfer coefficient, k_ga, in units of moles/(hr)(ft^3 column) (moles/ft^3). The k_ga range extends from 10,000 to 70,000. All other variables were at their respective base case conditions.

Figure 8

The effects of a variance in k_ga on the operating profit of the recovery system is shown in this figure. The range of k_ga is 10,000 to 70,000 moles/(hr)(ft^3 column) (moles/ft^3) and the base case k_ga is 20,000. Curves are plotted for SO_2 credit values of 0.5 cents/lb and 1.0 cents/lb.

Figure 9

In this figure, the SO_2 sorption batch time is plotted against the solid-gas interfacial equilibrium constant (H). The equilibrium constant is defined by the expression

$$C_i = HC_p$$

where C_i is the SO_2 concentration at the fluid-solid interface which is in equilibrium with C_p, the moles of SO_2 per lb of paper. The units for this constant are (moles SO_2/ft^3 gas)/(moles SO_2/lb paper).

The batch time was evaluated for H values ranging from 10^{-2} to 10^{-5} and, as shown, the batch time increases as the value of H decreases in magnitude. All other variables were at base case conditions.

Figure 10

This figure is a plot of the equilibrium constant, H, vs operating profit in terms of MM $/yr and $/ton coal. The base case condition in 0.001 (moles SO_2/ft^3 gas)/(moles SO_2/lb paper).

Figure 11

The effect of sorption column diameter on the SO_2 sorption batch time is illustrated in Figure 11. As expected, the batch time increases as the column diameter becomes larger. The base case diameter is 30 ft.

Figure 12

Figure 12 shows the effect of column diameter on the overall operating profit of the SO_2 recovery system. Curves are plotted for SO_2 credit value of 1.0 cents/lb and 0.5 cents/lb. All other values are at the base case operating conditions.

For the proposed SO_2 recovery system, the batch time decreases as the column height becomes smaller (Figure 11) but the amount of paper required by the sorption process becomes larger. Because the fuel credit value exceeds the initial cost, rising operating profits are realized as the amount of paper burned for fuel increases. Therefore, a trade-off results for, although the shorter column returns a larger margin of profit, problems related to obtaining a sufficient supply of paper and to regenerating the paper in the given time period will likely arise.

Figure 13

Figure 13 shows the effect of column height on the sorption batch time for columns having diameters of 30 feet and 40 feet. Besides indicating that batch time increases proportionately with column height, the plot also shows that the rate of increase in batch time (represented by the slope of the curves) is greater for the column 40 feet in diameter.

Figure 14

The effect of column height on the operating profit for a column 30 feet in diameter is shown in this figure. As shown, the operating profit decreases as the column height increases. With the substitution of column height for column diameter, the discussion presented for Figure 8 would also apply here.

Figure 15

This plot is similar to Figure 14 except that the curves correspond to a column 40 feet in diameter.

Figure 16

The effect of the weight of paper per cubic foot of column and void fraction (ft^3 actual volume/ft^3 empty column) on the sorption batch time is illustrated in Figure 16. The density of the paper (lbs paper/ft^3 paper) is assumed constant and thus the weight of paper per cubic foot of column and the fraction (values in parentheses) are related by

$$DEN = \rho/(1 - \epsilon)$$

when

DEN = lb./paper/ft^3 paper

ρ = lb paper/ft^3 column

ϵ = ft^3 actual volume/ft^3 empty column

As expected, the batch time increases as the amount of paper in the column increases.

Figure 17

Operating profit vs the weight of paper per cubic foot of column and void fraction are plotted in Figure 17. The numbers in parentheses along the abscissa of Figure 17 represent values for the void fraction. According to the plot, the weight of paper per unit column volume (and the void fraction) does not significantly affect the operating profit over the range analyzed.

Figure 18

Figure 18 shows the effect of the mole fraction of SO_2 in the flue gas being fed to the sorption column on the sorption batch time. As can be seen from the curve, the mole fraction of SO_2 in the feed flue gas has a significant effect on the batch time.

Figure 19

This is a plot of the mole fraction of SO_2 in feed flue gas vs the operating profit. The operating profits do increase as the SO_2 feed mole fraction becomes larger because the revenue from SO_2 recovery also increases. Although the operating profits improve with a high SO_2 mole fraction in the feed flue gas, batch time favors a low value for this parameter.

Figure 20

In Figure 20, the SO_2 sorption batch time is shown to increase as the SO_2 concentration of the paper (lbs SO_2/lb paper) at saturation conditions also increase.

Figure 21

Figure 21 illustrates curves relating the saturated SO_2 concentration of the paper to the operating profit of the proposed system. Again, the operating profits are highly dependent on the SO_2 credit value.

Figure 22

Figure 22 indicates the effect of an increase column diameter on the capital investment of the proposed SO_2 recovery process. All parameters, except column diameter, were at their respective base conditions.

Figure 23

The effect of column height on overall capital investment is shown in this figure. Two curves corresponding to the column diameters of 30 feet and 40 feet are plotted.

Figure 24

Figure 24 shows the inversely proportional relationship between the operating profit of the proposed SO_2 recovery process and the cost of paper. According to the plot, a process operating at the base case conditions will show a profit if the paper cost is less than 1.3 cents/lb.

Figure 25

This figure is a plot of the operating profit vs the percentage of paper replacement per sorption cycle. In the base case, 2% of the paper is replaced prior to SO_2 sorption. As the percentage of paper replacement increases, the practical problem of obtaining and handling sufficient amounts of paper becomes magnified. The slopes of the curves are positive because the base case operating conditions result in a paper fuel credit that exceeds the paper cost.

Figure 26

Figure 26 is similar to Figure 25 except that the heat credit has been altered from the base case condition of 50 cents/MM Btu to 25 cents/MM Btu. In this case, the fuel credit of the paper no longer exceeds the initial cost of the paper, and therefore the slopes of the curves are negative. If all other parameters except the heat credit are at their base case values, the proposed process will show a profit if the paper replacement per sorption cycle is less than 16%. The curves in both Figures 21 and 22 were calculated using 7560 Btu/lb paper as the heat of combustion of paper.

Figure 27

Figure 27 illustrates the effect of the SO_2 credit value on the operating profit of the SO_2 recovery system. The SO_2 credit value represents the net worth of SO_2 as a raw material fuel gas but does not include the cost of converting it to a salable product (i.e., sulfuric acid). A process operating at the base-case conditions will operate at a profit if the SO_2 credit value is greater than 0.2 cents per pound. If 100% sulfuric acid can be marketed at $20/ton (1 cent/lb of sulfuric acid or 1.5 cents/lb of SO_2), a profit can be realized if the cost of upgrading the SO_2 to sulfuric acid is less than 1.3 cents/lb of SO_2 (assuming all of the SO_2 sorbed on the paper is converted to sulfuric acid.

Figure 28

This figure is a plot of the heat credit value (cents/MM Btu) vs the operating profit. These curves are for the base case condition in which 2% of the paper in the column is used as fuel during each sorption cycle. The slope of the curve would increase if the percentage of paper replacement per sorption cycle was increased. The values of the operating profit were calculated assuming that the heat of combustion of paper is 7560 Btu/lb.

Figure 29

The curves in Figure 29 apply to a SO_2 recovery system employing a general sorbent material but otherwise similar to the proposed system. In this graph, the operating profit is plotted as a function of sorbent cost ($/hr). Zero heat credit was given to the sorbent in determining the curves and, therefore, the sorbent cost applies directly to a material which is discarded upon replacement. If the spent sorbent does have some economic worth, the value on the abscissa corresponds to the difference between the initial cost of the sorbent and any credit which can be assigned to the spent sorbent.

3.5 CONCLUSIONS

The results of the preliminary chemical systems analysis demonstrate that the proposed cellulose - SO_2 recovery process is economically feasible. Specifically the analysis computed that the process, operating at the selected base case conditions, will show a profit of $941,000 per year (42 cents/ton coal). This is a preliminary analysis of the proposed system and a more thorough determination of the values of the process parameters (probably by laboratory experimentation) is needed to substantiate these results.

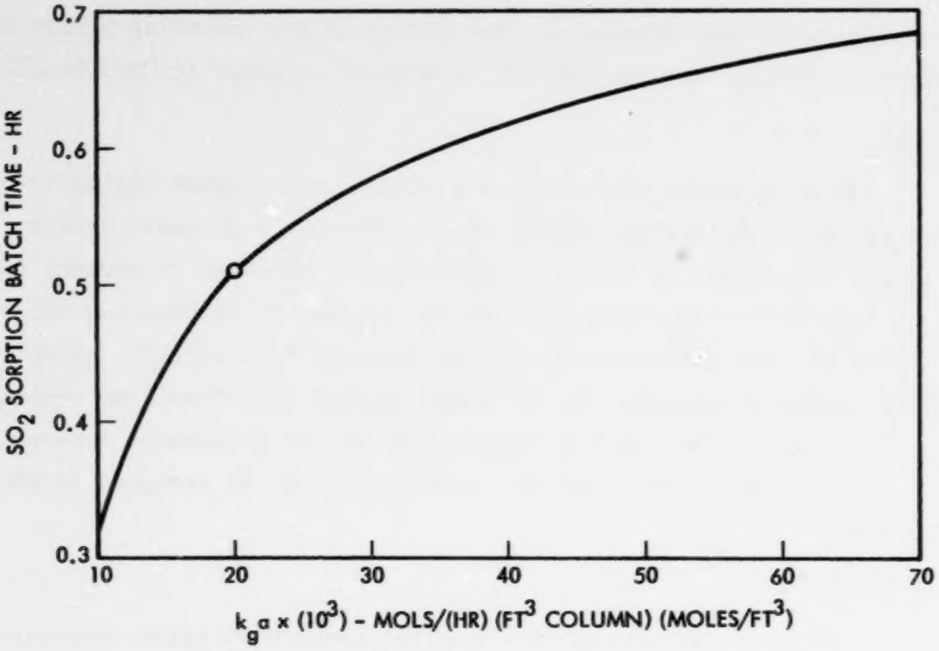

Figure 7. Effect of the Mass Transfer Coefficient on the SO_2 Sorption Batch Time

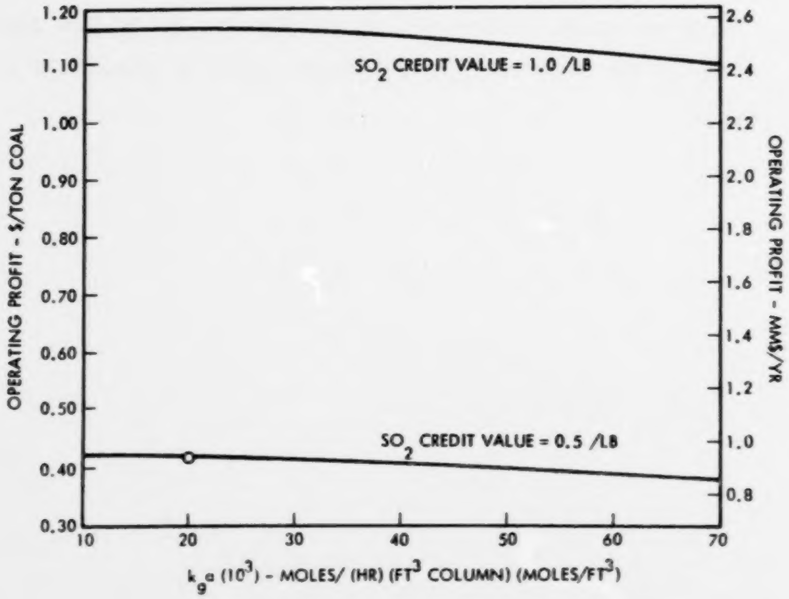

Figure 8. Effect of the Mass Transfer Coefficient on the Operating Profit of the SO_2 Recovery System

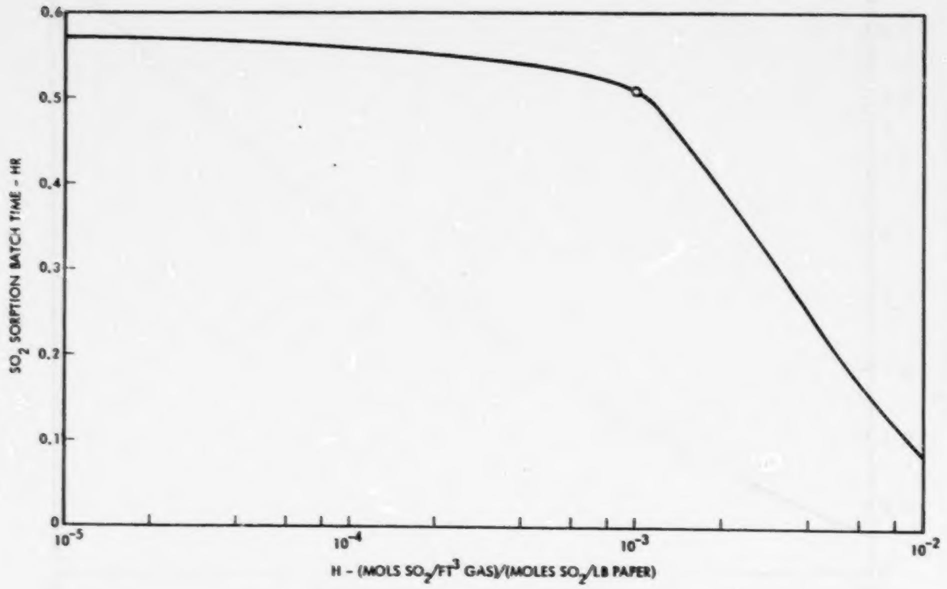

Figure 9. Effect of the Gas-Solid SO_2 Equilibrium Constant on the SO_2 Sorption Batch Time

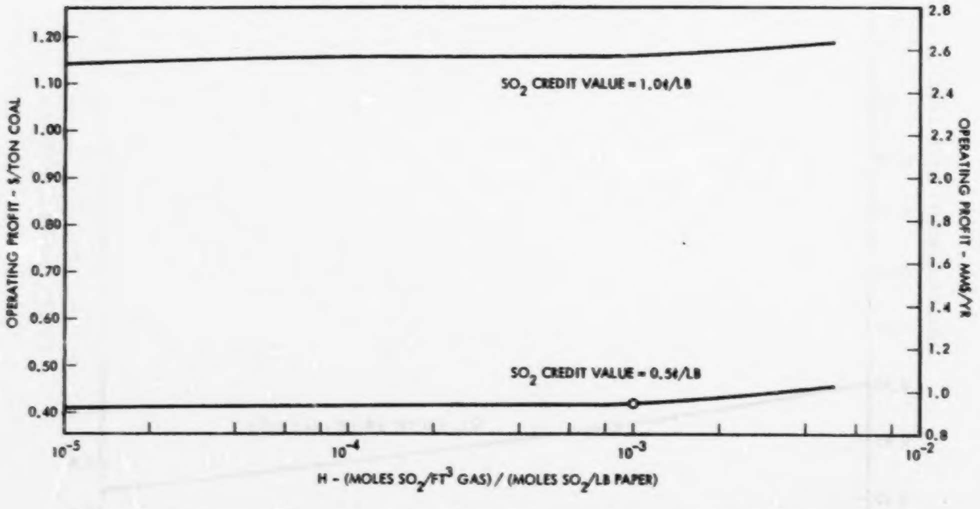

Figure 10. Effect of the Gas-Solid SO_2 Equilibrium Constant on the Operating Profit of the SO_2 Recovery System

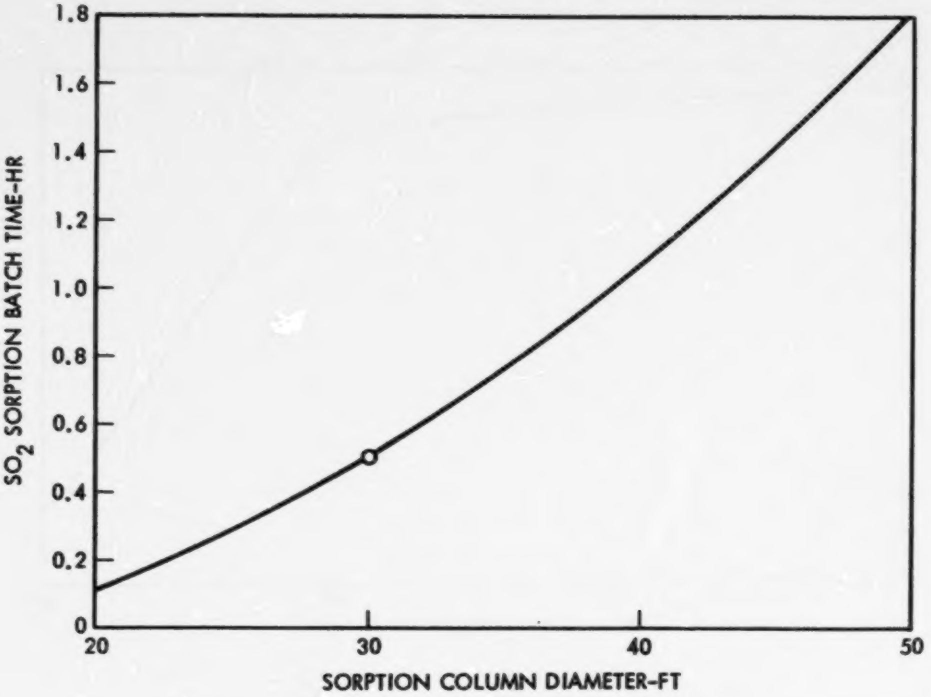

Figure 11. Effect of Sorption Column Diameter on the SO_2 Sorption Batch Time

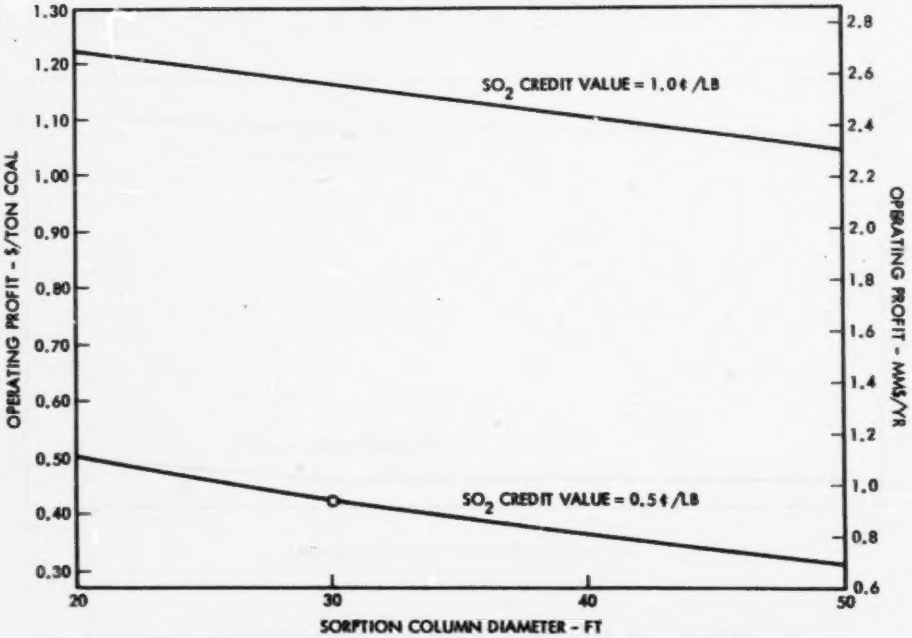

Figure 12. Effect of the Sorption Column Diameter on the Operating Profit of the SO_2 Recovery System

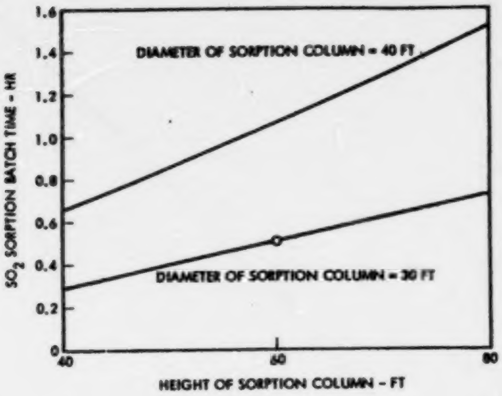

Figure 13. Effect of Sorption Column Height on the SO_2 Sorption Batch Time

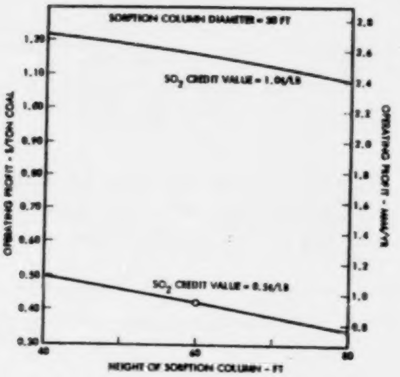

Figure 14. Effect of the Sorption Column Height on the Operating Profit of the SO_2 Recovery System (30-ft. col.)

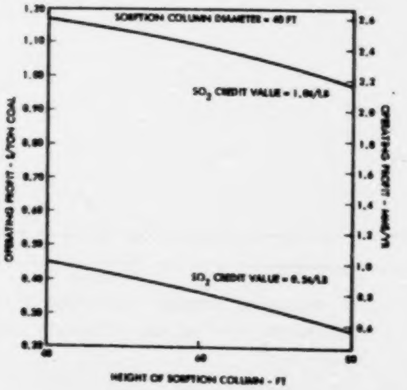

Figure 15. Effect of the Sorption Column Height on the Operating Profit of the SO_2 Recovery System (40-ft. col.)

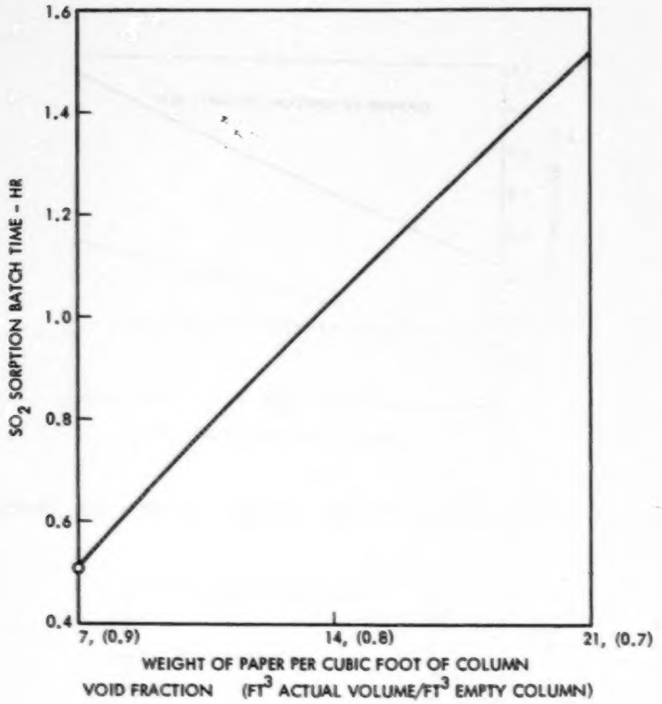

Figure 16. Effect of the Weight of Paper per Cubic Foot of Column and the Column Void Fraction on the SO_2 Sorption Batch Time

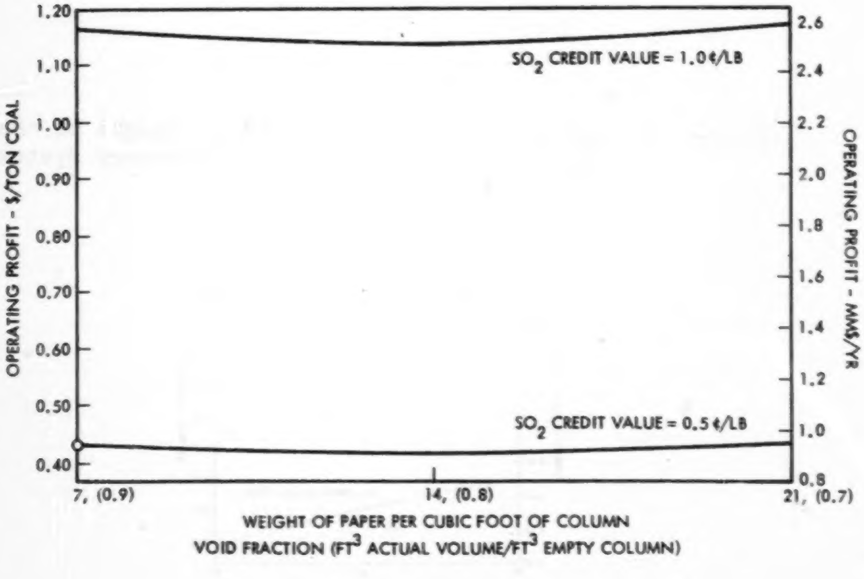

Figure 17. Effect of the Weight of Paper per Cubic Foot of Column and the Column Void Fraction on the Operating Profit of the SO_2 Recovery System

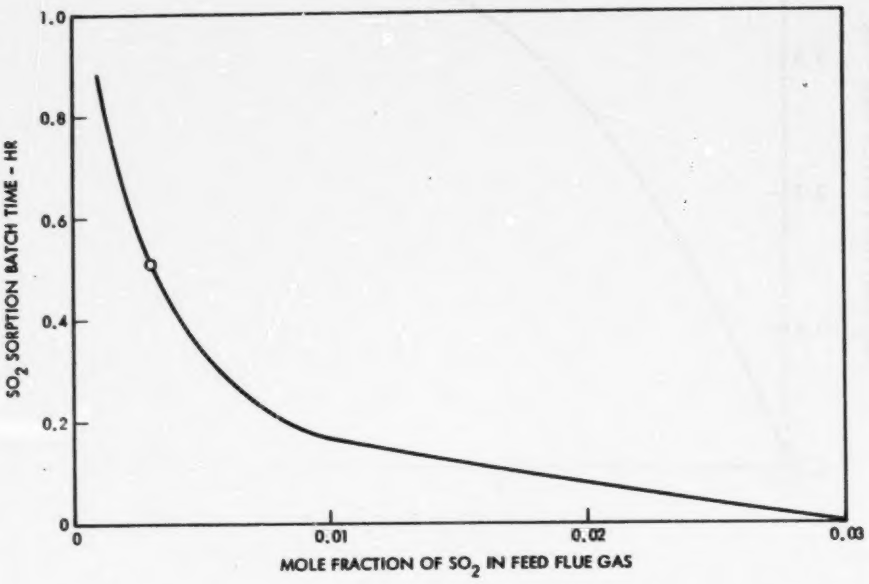

Figure 18. Effect of the SO_2 Mole Fraction in the Feed Flue Gas on the SO_2 Sorption Batch Time

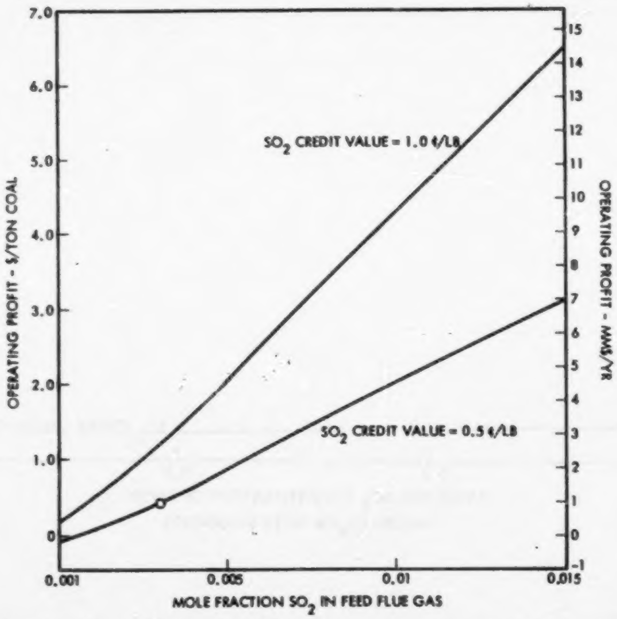

Figure 19. Effect of the SO_2 Mole Fraction in the Feed Flue Gas on the Operating Profit of the SO_2 Recovery System

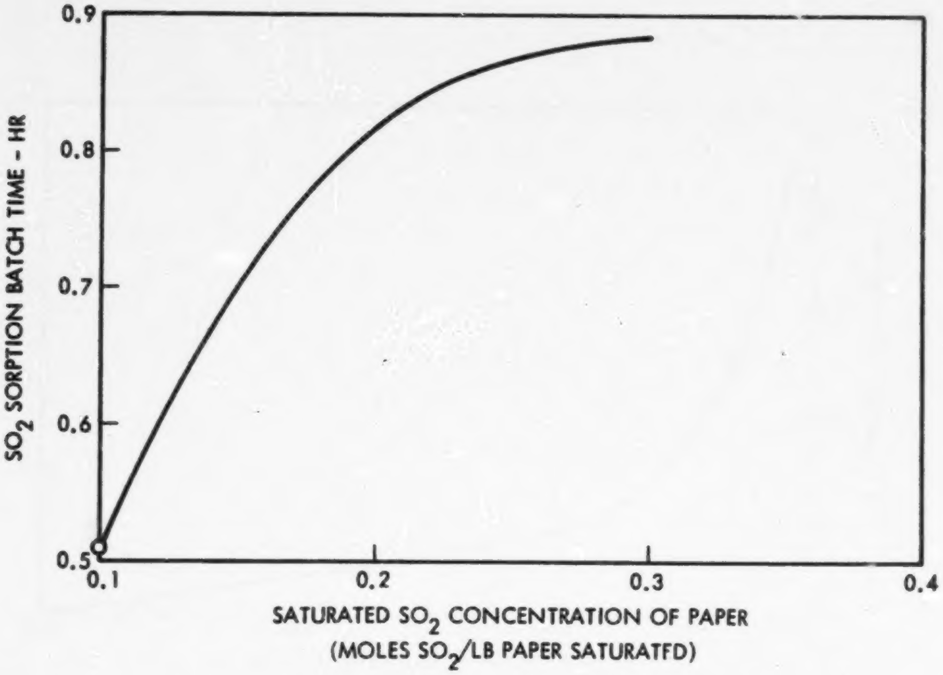

Figure 20. Effect of the SO_2 Concentration of the Paper at Saturation on the SO_2 Sorption Batch Time

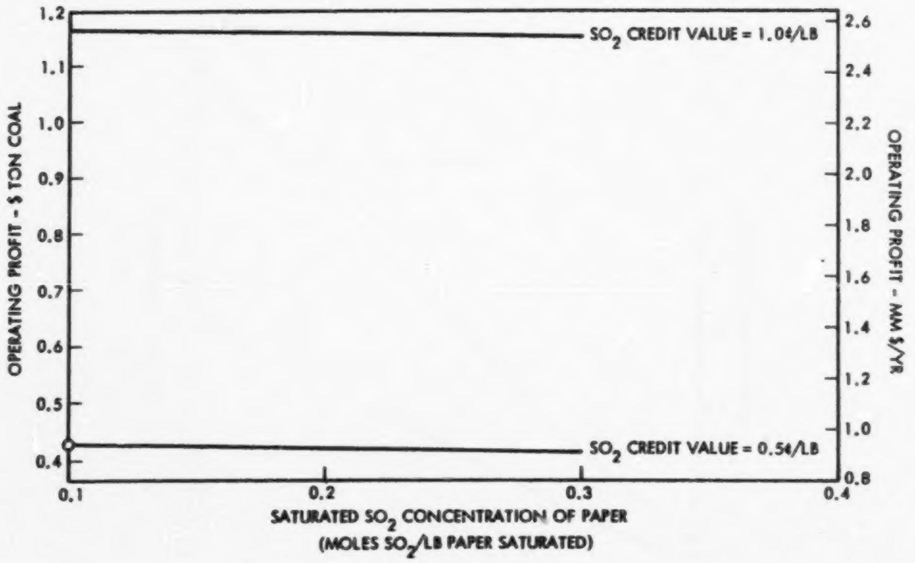

Figure 21. Effect of the SO_2 Concentration of the Paper at Saturation On the Operating Profit of the SO_2 Recovery System

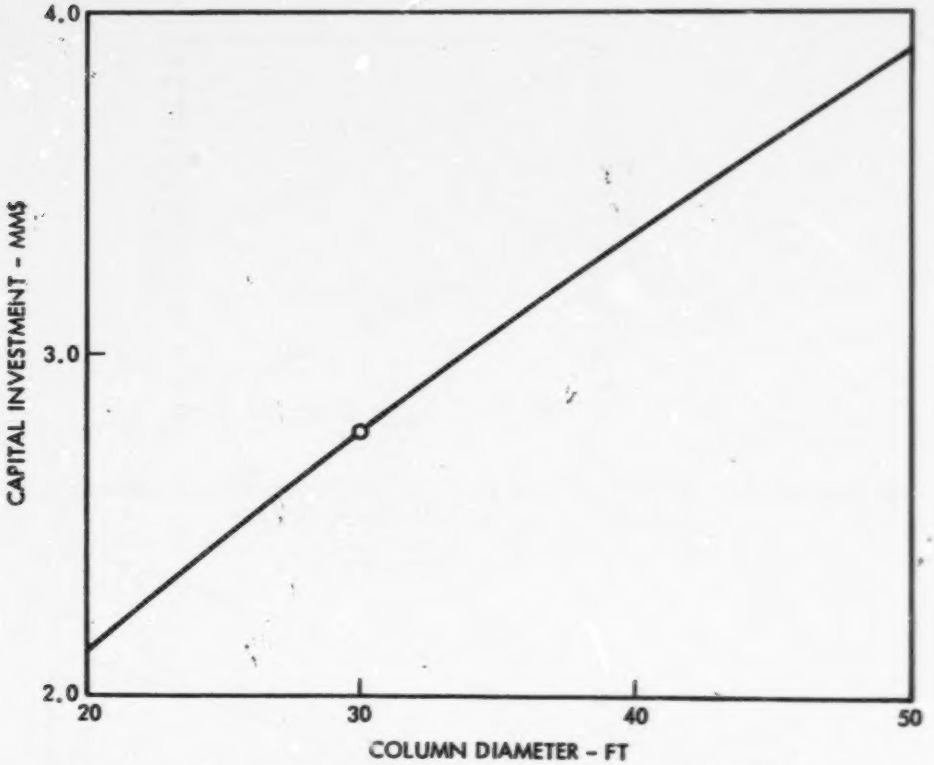

Figure 22. Effect of Column Diameter on the Capital Investment for the SO_2 Recovery System

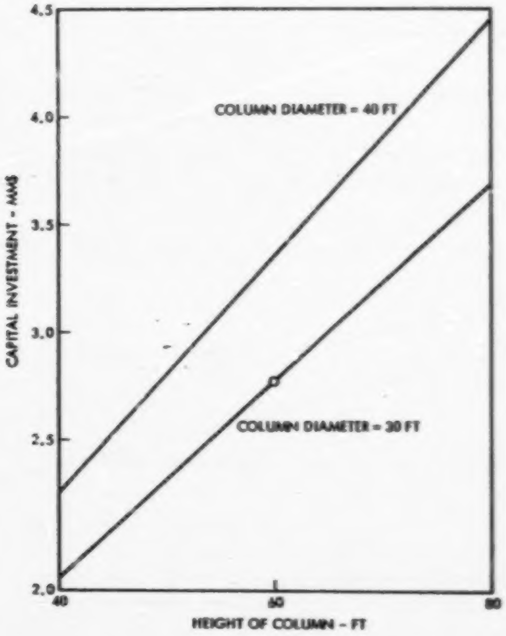

Figure 23. Effect of Column Height on the Capital Investment for the SO_2 Recovery System

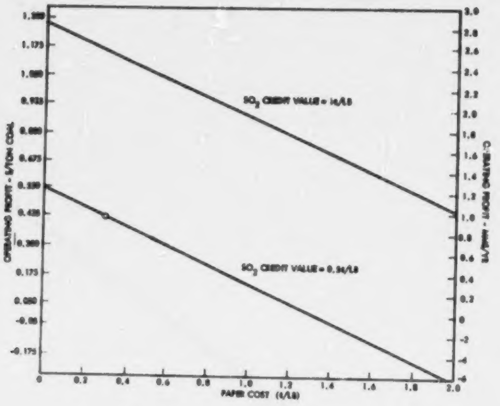

Figure 24. Effect of the Cost of Paper on the Operating Profit of the SO_2 Recovery System

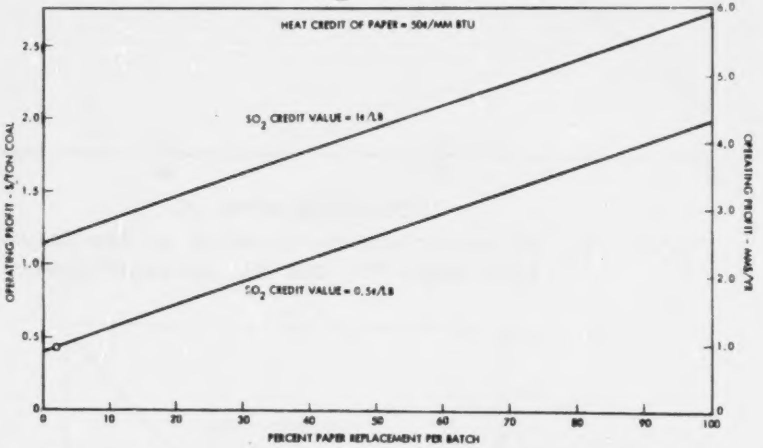

Figure 25. Effect of the Paper Replacement per Batch on the Operating Profit of the SO_2 Recovery System

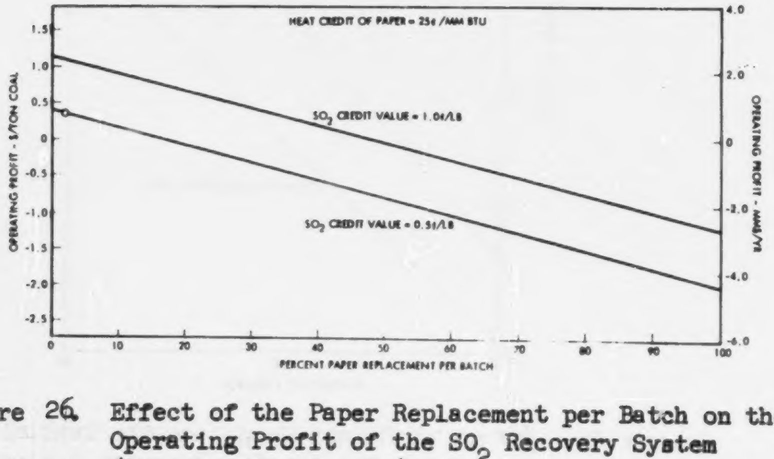

Figure 26. Effect of the Paper Replacement per Batch on the Operating Profit of the SO_2 Recovery System (Heat Credit Altered)

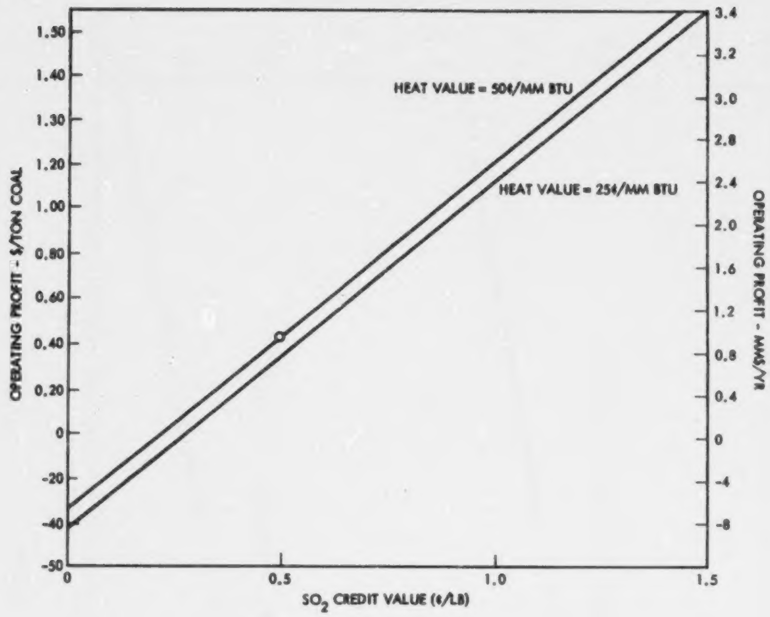

Figure 27. Effect of the SO_2 Credit Value on the Operating Profit of the SO_2 Recovery System

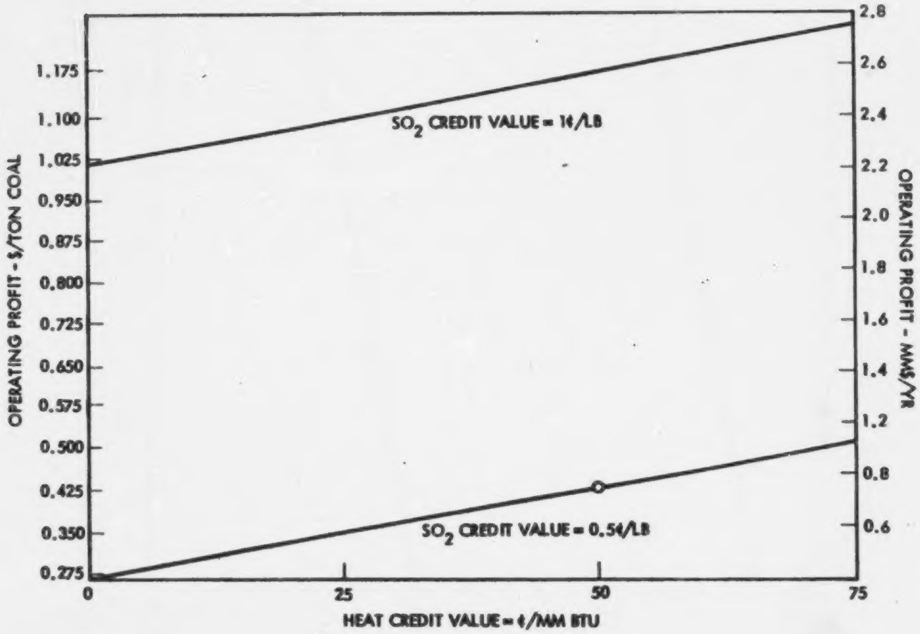

Figure 28. Effect of the Heat Credit Value on the Operating Profit of the SO_2 Recovery System

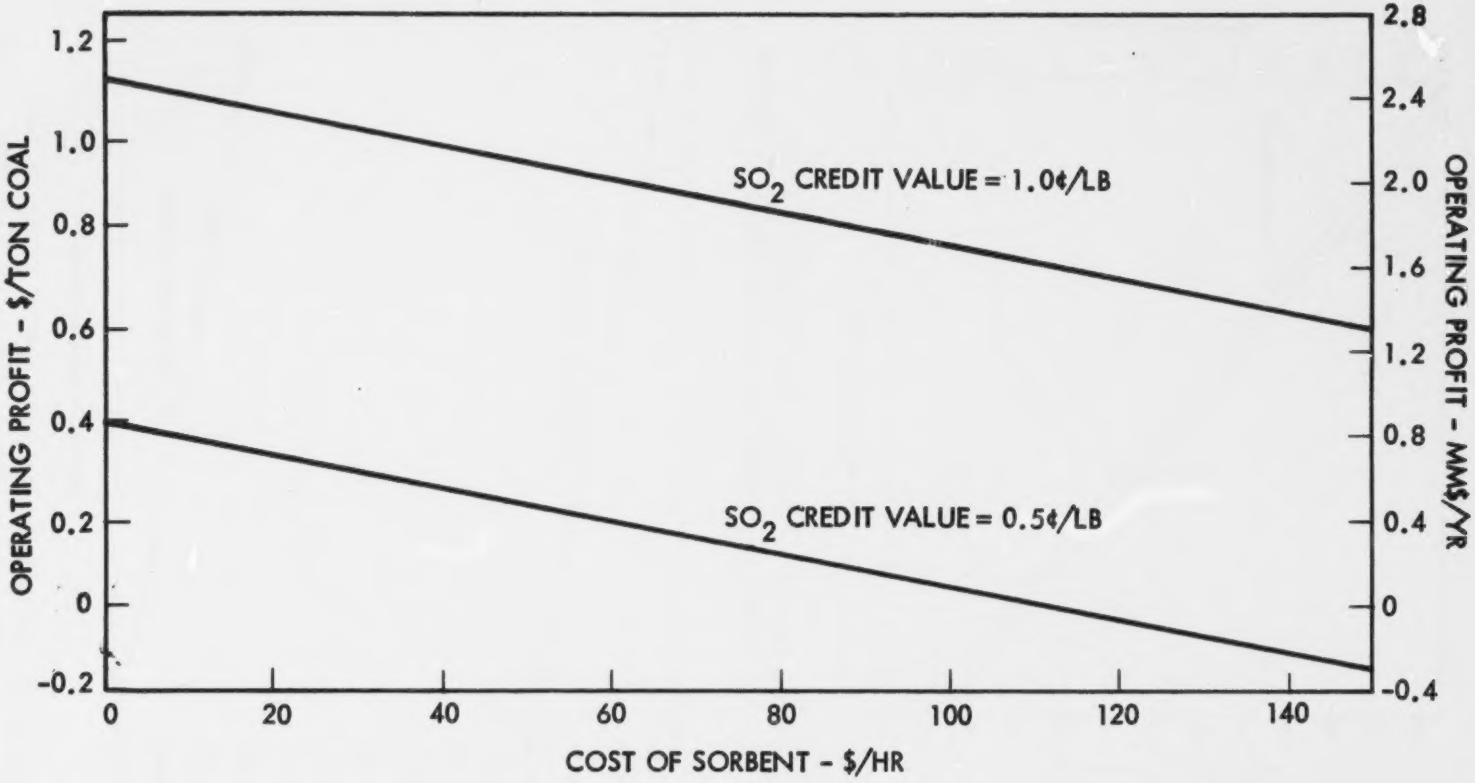

Figure 29. Effect of the Cost of a General Sorbent on the Operating Profit of the SO_2 Recovery System

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APPENDIX - COMPUTER PROGRAM LISTING

```
    DIMENSION X(201,2),Y(201,2),FX(201)
10  ACCEPT 15, AREA,ZFINAL,P,TEMP,FSC,S02PC,YFINAL,QSAT,DEN,E,XKG
15  FORMAT (4E12.6)
    CO = S02PC * P/(10.73 * (TEMP + 460.))
    Q = QSAT/64.
    G = FSC * 14.7 * (TEMP + 460.)/(P * 520. * AREA)
    SFINAL = E*ZFINAL/G
    TYPE 20, SFINAL
20  FORMAT(/E12.6,//,$INPUT - IS,IFLAG$,/)
    ACCEPT 25, IS,IFLAG
25  FORMAT (2I4)
    AH = SFINAL/IS
    AK = 1./60.
    CONY = (CO * XKGA)/(DEN * Q)
    CONX = (XKGA * H)/DEN
    CONST = (XKGA * H * Q)/(E * CO)
    TYPE 30, AK,AH,CONY,CONX,CONST
30  FORMAT(//5(E10.4,2X)//)
    IT = 1
    IS=IS+1
    THETA = 0.
    DO 100 N=1,IS
100 X(N,1) = 0.
    Y(1,1) = 1.
    DO 150 N=2,IS
150 Y(N,1) = 0.
200 S=0.
    ID=1
    Y(1,2) = 1.
    X1 = X(1,1)
    DX1 = CONY * Y(1,1) - CONX * X(1,1)
    DX=DX1
202 X(1,2) = X(1,1) + DX * AK
    IF((X(1,2)-X1) - 1.E-2)204,204,203
203 DX2 = CONY * Y(1,2) - CONX * X(1,2)
    DX = 0.5 * (DX1 + DX2)
    X1 = X(1,2)
    GO TO 202
204 IF(X(1,2)-1.)210,205,205
205 X(1,2)=1.
    Y(1,2)=1.
210 IF(IFLAG)225,225,215
215 IF(IT-30)225,220,220
220 TYPE 275, Y(1,2),X(1,2),S
225 DO 280 M=2,IS
    X1 = X(M,1)
    Y1 = Y(M-1,2)
    DX1 = CONY * Y(M,1) - CONX * X(M,1)
    DY1 = -(XKGA/E * Y(M-1,2) - CONST * X(M-1,2))
    DX=DX1
    DY=DY1
230 X(M,2) = X(M,1) + DX * AK
    Y(M,2) = Y(M-1,2) + DY * AH
    IF((X(M,2) - X1) - 1.E-2)235,235,240
235 IF((Y(M,2) - Y1) - 1.E-2)245,245,240
240 DX2 = C0NY * Y(M,2) - C0NX * X(M,2)
    DY2 = -(XKGA/E * Y(M,2) - C0NST * X(M,2))
    DX = 0.5 * (DX1 + DX2)
    DY = 0.5 * (DY1 + DY2)
    X1 = X(M,2)
    Y1 = Y(M,2)
    G0 T0 230
245 IF(X(M,2) - 1.)255,250,250
250 X(M,2) = 1.
    Y(M,2) = Y(M-1,2)
255 S=S+AH
    ID=ID+1
    IF(IFLAG)280,280,260
260 IF(IT-30)280,265,265
265 IF(ID-10)280,280,270
270 Z = S * G/E
    TYPE 275, Y(M,2),X(M,2),Z
275 F0RMAT (/3(1PE12.6,3X))
    ID=1
280 C0NTINUE
    THETA = THETA + AK
    IF(IT-30)320,300,300
300 T = THETA + E/G * ZFINAL
    TYPE 310, Y(IS,2),X(IS,2),T
310 F0RMAT (/1PE12.6,3X,1PE12.6,18X,1PE12.6//)
    IT = 0
320 IF(Y(IS,2) - YFINAL)330,400,400
330 D0 340 J=1,IS
    X(J,1) = X(J,2)
340 Y(J,1) =Y(J,2)
    IT = IT+1
    G0 T0 200
400 T = (THETA - AK) + E/G * ZFINAL
    IF(IFLAG)430,430,410
410 ZH=0.
    SH=0.
    D0 420 IA=1,IS,10
    TYPE 275, Y(IA,1),X(IA,1),ZH
    SH = SH + (AH * 10.)
420 ZH = SH * G/E
    TYPE 310, Y(IS,1),X(IS,1),T
430 D0 500 JA=1,IS
500 FX(JA) = X(JA,1) * Q * DEN * AREA
    AZ = ZFINAL/IS
    TS02 = 0.
```

```
      FX(IS+1)=0.
      JS=(IS+1)/2
      JS=2*JS
      DØ 510 KA=3,JS,2
  510 TSØ2 = TSØ2 + (FX(KA) + 4.* FX(KA-1) + FX(KA-2)) * AZ/3.
      VØL = AREA * ZFINAL
      PAPER = DEN * VØL
      TYPE 520, VØL,PAPER,T,TSØ2
  520 FØRMAT(////$VØL ABSØRBER - FT3$,5X,1PE12.6,/,$LBS PAPER
     1$,14X,1PE12.6,/,$BATCH TIME - HR$,8X,1PE12.6,/,$SØ2 REMØVED
     2 - MØLS$,5X,1PE12.6,//)
 4000 TYPE 5000
 5000 FØRMAT(///$INPUT PAPER CØST, SØ2 VALUE, HEAT CØST$/)
      ACCEPT 5010,PAPTØN,SØ2VAL,HTCST
 5010 FØRMAT(3F14.4)
      IDIA=0
      D=(AREA*4./3.1416)**0.5
      D=D*12.
      IF(D-200.)6020,6020,6010
 6010 DA=D
      D=200.
      IDIA=1
 6020 CØLCST=((((D*2.515E-06-8.899E-04)*D+0.1182)*D-1.079)*D+82.09)
     1*ZFINAL*2.93*2.0
      IF(IDIA)6030,6040,6030
 6030 CØLCST=CØLCST*((DA/D)**0.67)
 6040 PAPCST=PAPER*PAPTØN/2000./T
      PAPCR=PAPER*7560.*HTCST/1.0E+06/T/100.
      TØTCAP=3.5*CØLCST+3.5E+04
      CAPHR=0.2*TØTCAP/7920.
      SØ2CR=TSØ2*64.066*SØ2VAL/100./T
      ØPER=25.25
      REGEN=TSØ2*64.066*1000.*HTCST/1.0E+06/T/100.
      ØPCØST=PAPCST+CAPHR+REGEN+ØPER-PAPCR-SØ2CR
      TØTYR=ØPCØST*7920.
      PAPYR=PAPER*7920./2000./T
      SØ2YR=TSØ2*64.066*7920./2000./T
      TYPE 6000,TØTCAP,ØPCØST,SØ2CR,PAPCR,TØTYR,PAPYR,SØ2YR
 6000 FØRMAT(/////$SUMMARY$//$TØTAL CAPITAL CØST = $,3X,1PE14.6,
     1/$ØPERATING CØST $9H($/HR) = ,1PE14.6,/$SØ2 CREDIT $9H($/HR) = ,
     24X,1PE14.6,/$PAPER CREDIT $9H($/HR) = ,2X,1PE14.6,/$TØTAL YEARLY
     3CØST = $,4X,1PE14.6,/$PAPER USAGE (TØNS/YR) = $,1PE14.6,
     4/$SØ2 RECØVERED (T/YR) = $,1X,1PE14.6,/////)
      TYPE 6500
 6500 FØRMAT($MØRE ? $)
      ACCEPT 6600,IND
 6600 FØRMAT(I1)
      IF(IND)6700,6700,4000
 6700 CALL EXIT
      END
```

DIVISION II

PHASE II

Laboratory Screening and Detailed Accumulation of Data

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1.0 INTRODUCTION AND SUMMARY

This report division presents the Phase II activities for laboratory screening and detailed data collections. The laboratory effort had the following objectives:

- Screen selected organic solids for ability to remove sulfur dioxide from synthetic flue gas, and
- Obtain more detailed data on the most promising organic solid(s)

As a result of a detailed literature search and conceptual analysis during Phase I of this program, a number of organic solids were identified as having capacity for the binding of sulfur dioxide. A principle accomplishment of Phase I was the identification of a number of waste materials which have high potential for removal of sulfur dioxide from flue gases. Organic materials were selected on the basis of:

- Known or postulated ability to take up sulfur dioxide,
- Price and availability,
- Thermal stability,
- Regenerability, and
- Mechanical properties.

Five organic materials were selected which offer promise for removing sulfur dioxide from flue gases:

1. Cellulosics,
2. Nigrosin,
3. Poly(N-vinylcarbazole),
4. Pyrolyzed poly(vinylchloride), and
5. Pyrolyzed poly(acrylonitrile).

The specific cellulosics selected were: waste newsprint, sawdust and cotton. Although a number of other inexpensive cellulosic based materials could have been evaluated, the limitations of Phase II required that the scope be narrowed.

As little or no data was available regarding the ability of the above-mentioned organic solids to sorb sulfur dioxide, a screening program was initiated for the assessment of the relative potential of the selected organic solids for the removal of sulfur dioxide from flue gases. The screening program involved determination of thermal stability at flue gas temperature (215°F and above) and ability to take up sulfur dioxide from moving flue gas streams at 215° to 300°F. All seven candidates (this includes the three cellulosics) were found to be thermally stable in flue gas, while all but nigrosin were found to take up sulfur dioxide from synthetic flue gas streams. Of the solids which were evaluated, newsprint was found to be potentially the most promising offering the following advantages over other sorbent systems for removal of sulfur dioxide:

- Selective sorption of sulfur dioxide from flue gas streams. (Little or no pickup of nitrogen, water carbon dioxide, oxygen, etc).
- Low initial price (e.g., $3.00 per ton for office waste paper).
- The large scale use of waste cellulosics for sulfur dioxide removal could help solve a solid waste disposal problem.
- Ready availability of sorbent in areas proximate to power stations.
- High mechanical strength, e.g., tensile strength of 80,000 psi compared with 65,000 psi for medium steel.
- Reversible sorption.
- Low temperature regeneration (350°F).

More detailed accumulation of data was performed on newsprint utilizing synthetic flue gases at temperatures encountered in flue gas streams (215° - 300°F). Both thermogravimetric analysis of weight increases of newsprint as a function of time in synthetic flue gas and chemical analysis of flue gas streams which had passed through packed beds of newsprint were performed to determine rate and capacity of newsprint for SO_2 sorption. In addition, regeneration studies were performed utilizing chemical analysis of desorption streams. The results may be summarized as follows:

- Newsprint picks up approximately 1-2% by weight sulfur dioxide in 20 minutes at a flow rate of ca., 200 vol/hr.
- Newsprint has a capacity of approximately 10% SO_2 by weight.
- Desorption streams of 16-26% by volume sulfur dioxide are obtained from newsprint at desorption temperatures of 350-450°F.

The results of the screening tests and more detailed accumulation of data, together with experimental procedures are presented in four sections:

2.0 Screening of Organic Solids,

3.0 More Detailed Accumulation of Data on Newsprint,

Appendix A - Thermogravimetric Analysis of SO_2 Sorption and

Appendix B - Sorption-Desorption Experiments - Analysis of Effluent Flue Gas

2.0 SCREENING OF ORGANIC SOLIDS

Five organic solids were identified in a detailed literature search and conceptual analysis which offered promise for removing sulfur dioxide from flue gas streams:

- Cellulosics
- Nigrosin
- Poly(N-vinylcarbazole) - PVK
- Pyrolyzed poly(vinylchloride) - PVC
- Pyrolyzed poly(acrylonitrile) - PAN

The specific cellulosics selected for this study were: waste newsprint, sawdust, and cotton. The chemical compositions of the above candidates as well as the postulated chemical and physical interactions with SO_2 are discussed in detail in the Phase I report. A sequential screening program was designed in order to determine which of the candidates should undergo more detailed characterization (Figure 1).

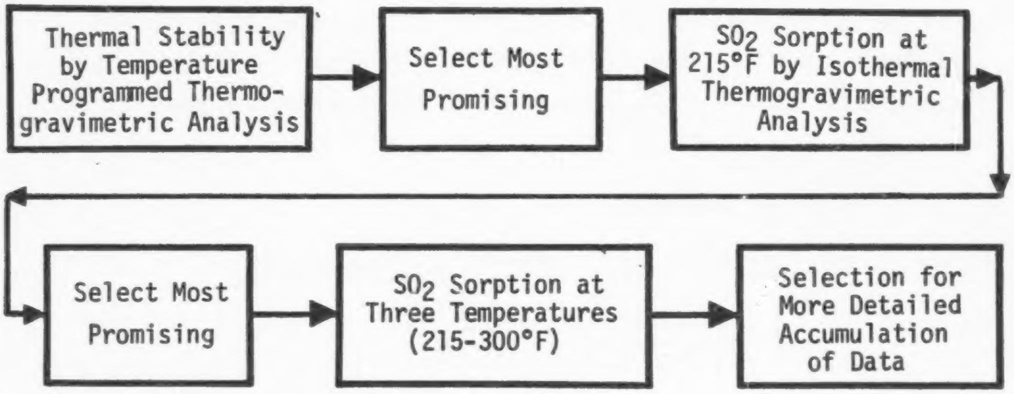
Thermal Stability by Temperature Programmed Thermogravimetric Analysis
Select Most Promising
SO2 Sorption at 215°F by Isothermal Thermogravimetric Analysis
Select Most Promising
SO2 Sorption at Three Temperatures (215-300°F)
Selection for More Detailed Accumulation of Data

FIGURE 1. SCREENING OF ORGANIC SOLIDS

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Thermogravimetric analyses in air and in synthetic flue gas were identical (Figure 2) and showed that all of the candidates were stable at flue gas temperatures. Two types each of pyrolyzed PVC and Nigrosin were evaluated.

The next sequential screening step involved measurement of weight uptake by temperature programmed thermogravimetric analysis in a synthetic flue gas. The flow rate was constant at 100 cc/min and it was assumed that weight uptake was due to sulfur dioxide (this was verified for newsprint and sawdust). All candidates were initially screened at 215°F. Poly(vinylcarbazole), sawdust, pyrolyzed poly(acrylonitrile), and newsprint picked up significant quantities of sulfur dioxide (Table I). At this point, those organic solids which failed to pick up weight were eliminated (with the exception of cotton, as the cellulosics as a class had shown weight uptake to 215°F and it was thought possible that the cotton might show an improved weight uptake at elevated temperatures). In addition, poly(vinylcarbazole) was eliminated even though it took up sulfur dioxide because of its high price, e.g., in order for the PVK to be a candidate for further investigation, it would have had to show a marked improvement over the other far less expensive organic solids.

The next screening step involved determination of sulfur dioxide uptake at four temperatures (Table II). Cotton, newsprint, sawdust, and pyrolyzed PAN picked up weight at temperatures of 215-300°F. The cellulosics did not pick up weight in some of the temperature regions, probably due to the operability of more than one sorption mechanism (Eqs. 1 and 2). Table III shows the regenerable uptake of SO_2 by newsprint and sawdust as compared with activated charcoal.

CHARGE TRANSFER

$$\text{CELLULOSE} + n\,SO_2 \rightleftharpoons \text{CELLULOSE}\cdot(SO_2)_n$$

$$K_{equil} = \frac{\left[\text{CELLULOSE}\cdot(SO_2)_n\right]^n}{\left[\text{CELLULOSE}\right]\left[SO_2\right]^n} \qquad (1)$$

CHEMICAL REACTION

$$\text{CELLULOSE}-(\text{OH})_n + nSO_2 \rightleftharpoons \text{CELLULOSE}-(\text{OSO}_2\text{H})_n$$

$$K_{equil} = \frac{\left[\text{CELLULOSE}-(\text{OSO}_2\text{H})_n\right]^n}{\left[\text{CELLULOSE}-(\text{OH})_n\right]\;\left[SO_2\right]^n} \qquad (2)$$

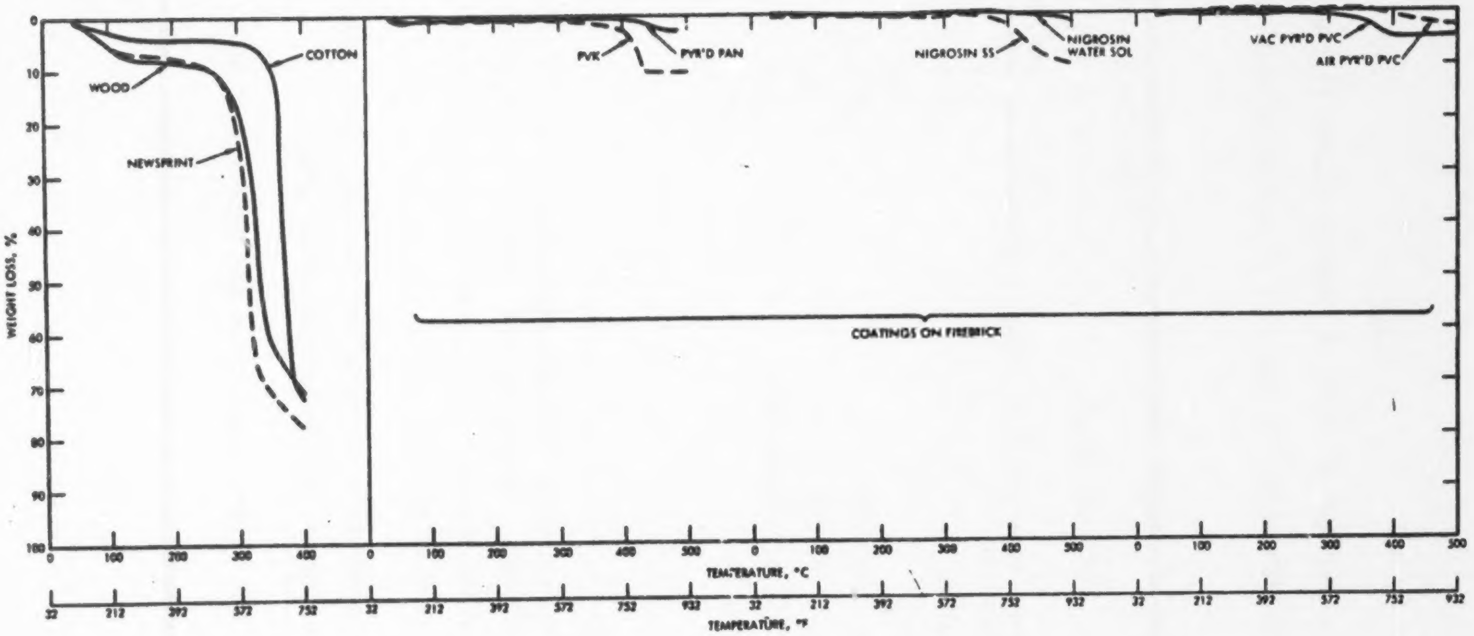

FIGURE 2. Thermogravimetric Analyses of Organic Solids in Air or in Synthetic Flue Gas

TABLE I

SO_2 SORPTION AT 215°F OF ORGANIC SOLIDS BY ISOTHERMAL THERMOGRAVIMETRIC ANALYSIS IN SYNTHETIC FLUE GAS[a]

ORGANIC SOLID	% UNCORRECTED WEIGHT UPTAKE OF SO_2[b,c] in 3 hr. periods
Newsprint	1.9
Sawdust	3.0
Cotton	-0-
Pyrolyzed PVC	2.2
Pyrolyzed PAN	-0-
Poly(N-vinylcarbazole)	3.0
Nigrosin	-2.0

---

[a] The synthetic flue gas with composition: 0.57% SO_2, 0.07% NO_2, 18.07% CO_2 and 2.80% O_2 was humidified by passage through a humidifier maintained at 40°C. Flow rate was 100 cc/min.

[b] No correction was made for the slow thermal loss of the organic solids maintained at 215°F.

[c] Weight uptake taken to be due entirely to SO_2.

TABLE II

SO_2 SORPTION AT FOUR TEMPERATURES OF ORGANIC SOLIDS BY ISOTHERMAL THERMOGRAVIMETRIC ANALYSIS[a]

ORGANIC SOLID	TEMP °F	UNCORRECTED % WEIGHT UPTAKE OF SO_2[b] in 3 hr. time periods	
Newsprint	215	1.9	2.6[c]
	250	-0-	0.9[c]
	275	1.8	2.8[c]
	300	-0-	1.0[c]
Cotton	215	-0-	
	250	0.5	
	275	-0-	
	300	0.4	
Sawdust	215	3.0	
	250	-0-	
	275	-0-	
	300	-0-	
Pyrolyzed PAN	215	2.2	
	250	1.9	
	275	3.2	
	300	1.4	

---

[a] The synthetic flue gas with composition: 0.57% SO_2, 0.07% NO_2, 18.07% CO_2 and 2.80% O_2 was humidified by passage through a humidifier maintained at 40°C. Flow rate was 100 cc/min.

[b] Weight uptake taken to be due entirely to SO_2.

[c] Corrected weight %, correction factors determined from isothermal runs in nitrogen: + 0.23%/hr. at 215°F, + 0.30%/hr. at 250°F, + 0.32%/hr at 275°F + 0.33%/hr. at 300°F.

TABLE III. SO_2 Uptake of Cellulosics and Charcoals

Sorbent	Surface Area m^2/g	Initial SO_2 Uptake [(a, d)]		Regeneration I[(a, b, d)]		Regeneration II[(a, b, d)]	
		g/g sorb. x 10^{-2}	g/m^2 sorb. x 10^{-2}	g/g sorb. x 10^{-2}	g/m^2 sorb. x 10^{-2}	g/g sorb. x 10^{-2}	g/m^2 sorb. x 10^{-4}
Sawdust	0.5[(c)]	5.9	11.8	4.0	8.0	4.3	8.6
Newsprint	1.3[(c)]	4.0	3.1	4.6	3.5	5.0	3.9
Activated Charcoal	1000 (Approx)	7.9	.0079	--	--	--	--
Carbon Black	--	0	--	--	--	--	--

(a) 30% SO_2 in N_2 stream through sorbent at 215°F space velocity approximately 25 hr^{-1} (neglecting volume occupied by sorbent)

(b) N_2 stream at 350°F for 5 minutes, space velocity approximately 250 hr^{-1} (neglecting volume occupied by sorbent)

(c) BET method with Krypton

(d) SO_2 uptake was determined by first passing a very small amount of N_2 gas through material at room temperature to remove unsorbed and loosely bonded SO_2, then flushing with N_2 at 350°F passing effluent through std. base and back titrating with H_2SO_4.

3.0 MORE DETAILED ACCUMULATION OF DATA ON NEWSPRINT

At this point, newsprint was selected as the prime candidate due to the fact that it had a leading weight uptake and was, by far, the least expensive and most easily obtainable in quantity of all the organic solids in contention. More detailed determination of rate of sorption of sulfur dioxide as a function of temperature and sulfur dioxide concentration was determined for newsprint by thermogravimetric analysis (Table IV).

It should be indicated that while the TGA technique, as applied to cellulosics for SO_2 uptake, is exploratory in nature, a definite increase in weight of cellulosics in synthetic flue gas is noted, which clearly shows affinity of the specific cellulosic materials for SO_2 at flue gas temperature.

The results indicate that paper picks up sulfur dioxide from flue gas streams containing 0.57-2.0% v/v sulfur dioxide at temperatures of 215-302°F with an ultimate capacity for sulfur dioxide of 10.2% by weight. The rate data shown in the tables were obtained under diffusion limited conditions at approximately 10 vol/hr^{-1} wherein the laminar layer about the paper sample greatly influences the rate of diffusion controlled sorption of SO_2.

Sorption and desorption profiles were determined for packed beds of shredded newsprint. Synthetic flue gas was passed through a packed bed of paper maintained at 215°F at a velocity of 180 vols/hr for a period of 20 minutes. The sorption of SO_2 from the stream was followed by chemical analysis of the effluent flue gas. The results are shown in Figures 3 and 4. The figures show initial rapid uptake of sulfur dioxide during the first five to six minutes of sorption followed by a slower but indeed, significant uptake out to the termination of the experiment.

Desorption of sulfur dioxide from newsprint was found to give 22-26% v/v SO_2 in the desorption gas stream at 450°F and 16.5% maximum percent SO_2 v/v in the desorption gas stream at 350°F (See Table V).

TABLE IV

DETERMINATION OF RATE OF SORPTION OF SULFUR DIOXIDE BY NEWSPRINT AS A FUNCTION OF SULFUR DIOXIDE CONCENTRATION AND TEMPERATURE

RUN NO.	SO_2 CONTENT	TEMP., °F	CORRECTED[a, b] $\Delta W/\Delta t$, mg/hr	TOTAL % WEIGHT UPTAKE OVER 7 HOUR PERIOD
1	0.57% (0.0149 mg/ml)	216	1.74	---
2		248	2.00	---
3		302	0.62	---
4	1.0% (0.0262 mg/ml)	216	2.34	---
5		248	0.81	---
6		302	0.38	---
7	2.0% (0.0524 mg/ml)	216	4.20	---
8		248	1.77	---
9		302	1.59	---
10	0.57% (0.0149 mg/ml)	216	2.48	---
11		216	----	10.2[d]

---

[a] Correction factors for paper weight loss at temperature, determined in dry nitrogen (+ 0.67 mg/hr at 215°F, + 0.87 mg/hr at 248°F and + 0.95 mg/hr at 302°F).

[b] 100 cc/min flue gas flow for three hour time period the rate remains constant. Synthetic flue gas passed through humidifier at 40°C.

[c] Weight newsprint, approx. 290 mg.

[d] This sample was exposed to flue gas until rate leveled off to zero for ultimate capacity determination.

TABLE V

DESORPTION OF SO_2 FROM NEWSPRINT

DESORPTION - RUN 1[a] (450°F)				*DESORPTION - RUN 2[a] (450°F)*				*DESORPTION - RUN 3[a] (350°F)*			
Sample	Time of Flow, Min	% Volume SO2 in Effluent Gas	SO_2 (mg)	Sample	Time of Flow, Min	% Volume SO2 in Effluent Gas	SO_2 (mg)	Sample	Time of Flow, Min	% Volume SO2 in Effluent Gas	SO_2 (mg)
Preflow	(Expansion)	26.49	115.17	Preflow	(Expansion)	21.90	57.50	Preflow	(Expansion)	16.50	40.00
1	1	4.33	16.48	1	1	13.00	20.58	1	1	12.30	15.58
2	2	1.08	13.23	2	1	9.20	17.82	2	1	9.60	16.10
3	2	0.36	2.24	3	1	4.80	10.43	3	1	3.60	7.74
4	1	0.47	1.50	4	1	1.70	4.10	4	1	4.10	8.48
5	1	1.27	0.54	5	1	1.00	2.30	5	1	0.90	2.08
6	1	0.98	0.86	6	1	1.50	3.62	6	1	1.70	3.94
7	1	0.45	0.45	7	1	0.70	1.66	7	1	0.70	1.63
8	1	0.36	1.28	8	1	1.10	2.43	8	1	0.80	1.76
9	1	0.32	0.38	9	1	0.70	1.44	9	1	0.60	1.31
10	1	0.28	0.29	10	1	0.60	1.47	10	1	0.70	1.38
11	1	0.17	0.19	11	1	0.50	1.12	11	1	0.50	1.06
12	1	0.11	0.48	12	1	0.80	1.66	12	1	0.50	1.06
13	1	0.13	0.29	13	1	0.50	1.12	13	1	0.30	0.80
				14	1	0.20	0.70	14	1	0.40	0.90
				15	1	0.20	0.70	15	1	0.30	0.80

[a] Conditions

	Run 1	Run 2	Run 3
Col. length	8 ft	8 ft	8 ft
Ullage	102 cc	102 cc	102 cc
Total Volume	109 cc	110 cc	111 cc
Weight Newsprint	9.73 g	8.32 g	8.32 g
Bulk Density	1.28 g/cc	1.04 g/cc	1.04 g/cc
Regen. Temperature	450°F	450°F	350°F

SO_2 sorption stream for these experiments was a 30% SO_2 in nitrogen mixture.

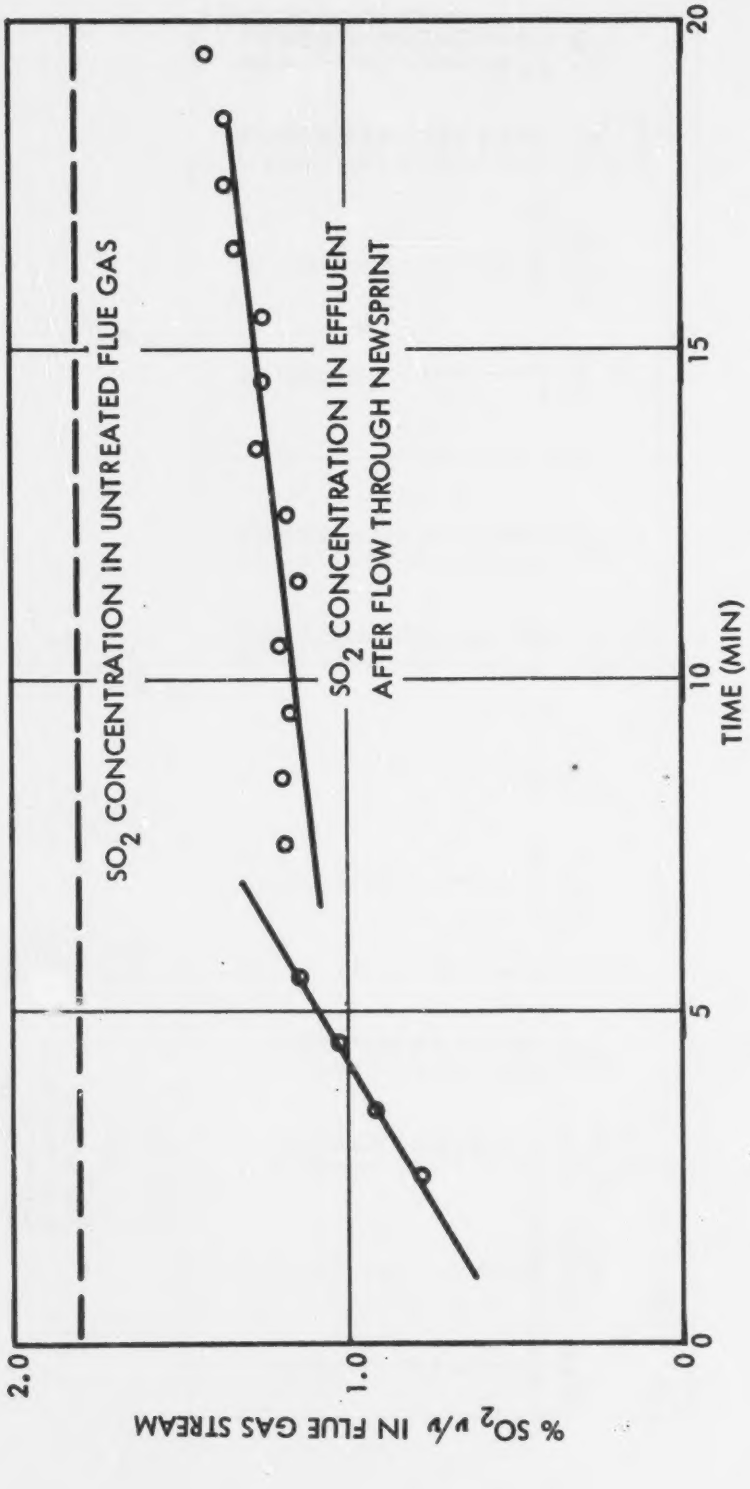

FIGURE 3. SO$_2$ CONCENTRATION IN FLUE GAS EFFLUENT

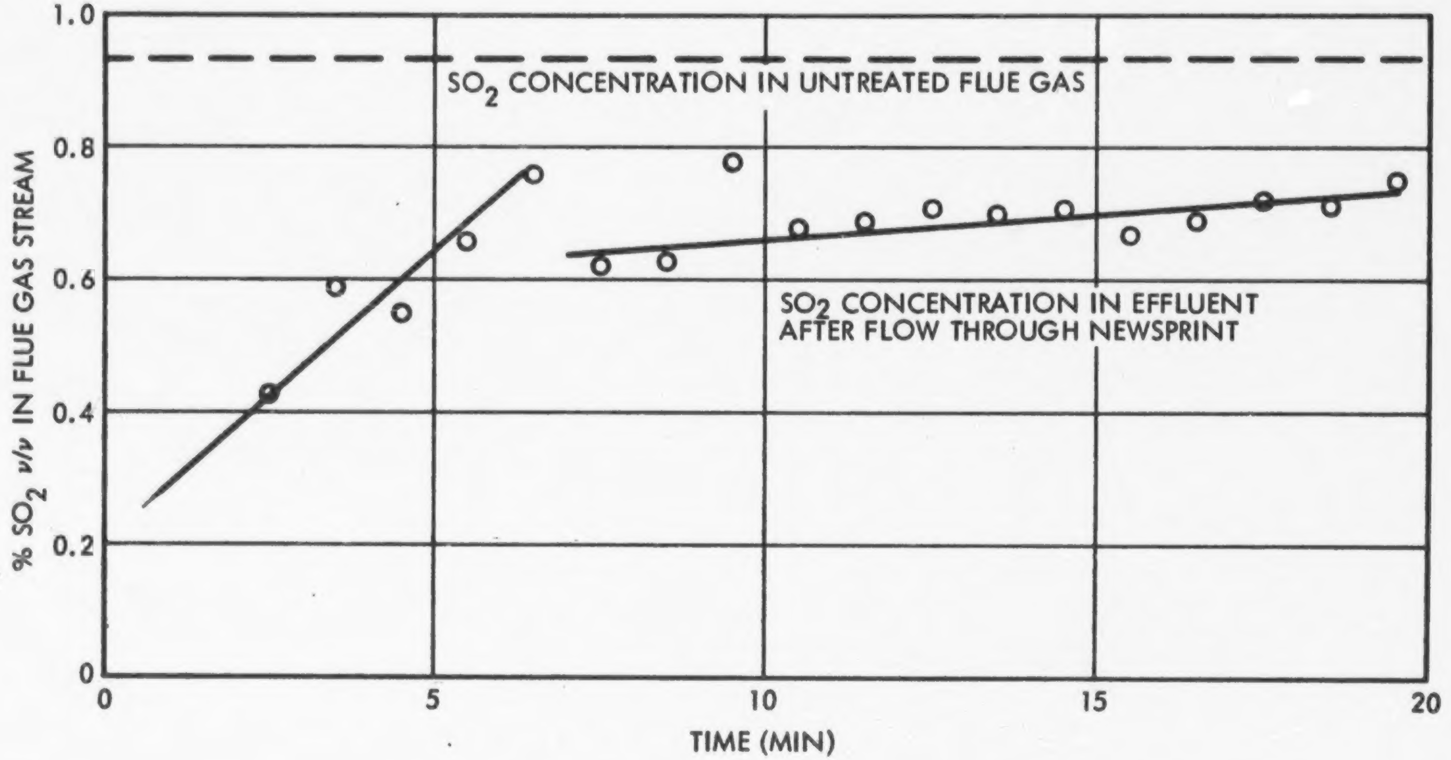

FIGURE 4. SO_2 CONCENTRATION IN DRY GAS EFFLUENT

APPENDIX A - THERMOGRAVIMETRIC ANALYSIS OF SO_2 SORPTION

A thermogravimetric analysis apparatus (TGA) was employed to monitor the changes in weight of samples of newsprint as a simulated "flue gas" was passed over the paper under isothermal conditions. The rate of weight gain was recorded as a function of time on an X-Y recorder. The weight gain data was employed to determine sorption rates at various temperatures.

An Aminco TGA was employed for the measurements of weight change. The simulated flue gas was prepared by passing a dry gas of the proper composition through a humidification chamber, where the gas stream was saturated with water vapor at the temperature maintained by the surrounding oven (40°C in this study). The lines from the oven to the TGA apparatus were insulated and heated to a temperature above the temperature maintained by the oven in order to prevent condensation of water in the lines. The gas flow into the humidification chamber was maintained at 100 cm^3 per minute by a metering valve. This flow rate provided a quantity of SO_2 which was greatly in excess of the quantity sorbed in any given time period.

The standard sample holder (Figure 5) was used for screening, while a special sample holder (Figure 6) was fabricated for the TGA balance for more detailed accumulation of data experiments. This holder is essentially a glass cage and suspension rod designed to maintain the sample in the desired cylindrical geometry throughout the experiment. The gas flow enters the furnace tube from the inlet tube at the bottom, passes around the sample, and exists from the apparatus.

The synthetic flue gas mixtures containing 1% and 2% SO_2 were prepared from the stock mixture purchased from Matheson, which has been described above, by adding down pressures of pure SO_2 to a storage tank, then filling to the required final pressure with the purchased flue gas mixture containing 0.57% of SO_2. A sufficient quantity of gas mixture was prepared at each SO_2 concentration to complete the scheduled runs at that composition. This method of preparing the synthetic flue gas supply was preferred to the method of mixing metered flows of component gases because of the greater certainty of maintaining a known gas composition throughout each experimental run.

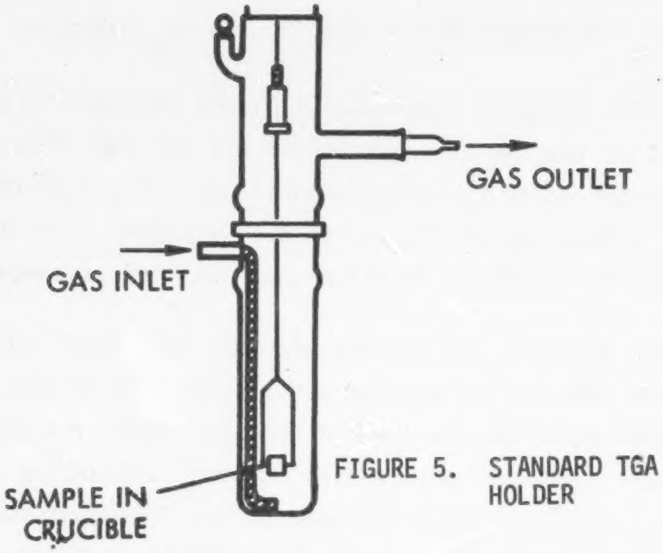

FIGURE 5. STANDARD TGA SAMPLE HOLDER

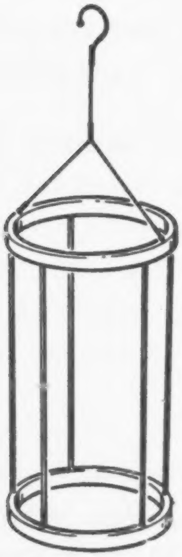

FIGURE 6. QUARTZ CAGE FOR ISOTHERMAL TGA EXPERIMENTS

The samples were rectangular pieces of newsprint 70. mm (2.8 inches) by 80. mm (3.1 inches). No preconditioning of any kind was carried out. Each sample weighed approximately 290 mg (6×10^{-4} lbs) with the exception of the capacity run for which a 550 mg sample was utilized.

Results

A series of 10 TGA runs of 3 hours duration were carried out at 102°C (115°F), 120°C (248°F), and 150°C (302°F) at the SO_2 concentrations of 0.57, 1.0 and 2.0 volume percent. In addition to these runs, a single run of 10 hours duration was carried out at 102°C and an SO_2 concentration of 0.57 volume percent. Data from all eleven TGA runs are tabulated in Table IV.

Correlation of rate of weight gain with increasing SO_2 concentration was generally masked by variations in paper surface characteristics such as, variations in amount of ink. Consequently, it was evident that further treatment of the data, such as calculation desorption kinetics or activation energies was not warranted.

The approximate capacity of the newspaper form of cellulosic was determined by TGA in run 11. For this determination, sample size was maximized (551 mg) maintaining 100 mg full scale on the TGA apparatus balance.

APPENDIX B - SORPTION-DESORPTION EXPERIMENTS - ANALYSIS OF EFFLUENT FLUE GAS

Experimental work was performed on packed columns of paper pulp. The sorption profiles reveal large initial sorption with lower level sorption continuing for the duration of the 20-minute runs. The desorption profiles indicate that a high percentage of the sorbed SO_2 is desorbed by a thermal mechanism and that repeated use of the columns are possible.

Sorption Experiments

The test apparatus utilized in the sorption experiments is presented schematically in Figure 7. The system consisted of two cylinders containing N_2 gas and synthetically-blended flue gas, respectively, a Fischer-Porter flowmeter, a metering valve, a humidifier (omitted for Run Number 2), a two-way valve, the sorption column system, the column by-pass system, an oven with an upper temperature limit of 400°C, a two-way stopcock, two pyrex glass scrubber traps, a bubble meter, and the necessary stainless steel lines and valves to construct the diagrammed system. The sorption experiments were conducted by the following procedure:

a. The system is constructed as diagrammed.

b. The oven temperature is allowed to reach equilibrium at the required sorption temperature.

c. The flow rate is established using flue gas through the by-pass system to determine approximate pressure and valve settings.

d. The scrubber traps were filled with 150 cc of 3% H_2O_2 solution.

e. The column valves are opened and the flue gas flow is diverted through the column system. Timing begins when flow is seen in the scrubber system.

f. Utilizing the two-way stopcock, the flue gas flow from the column is diverted to a fresh scrubber trap at one-minute intervals. During the one-minute periods, the scrubber trap is removed from the system, the sample recovered and fresh peroxide replaced in the trap. Once during each interval, a flow rate reading is taken.

g. Sampling continues at one-minute intervals for 20 minutes. The samples are analyzed by the procedure given in the following paragraph.

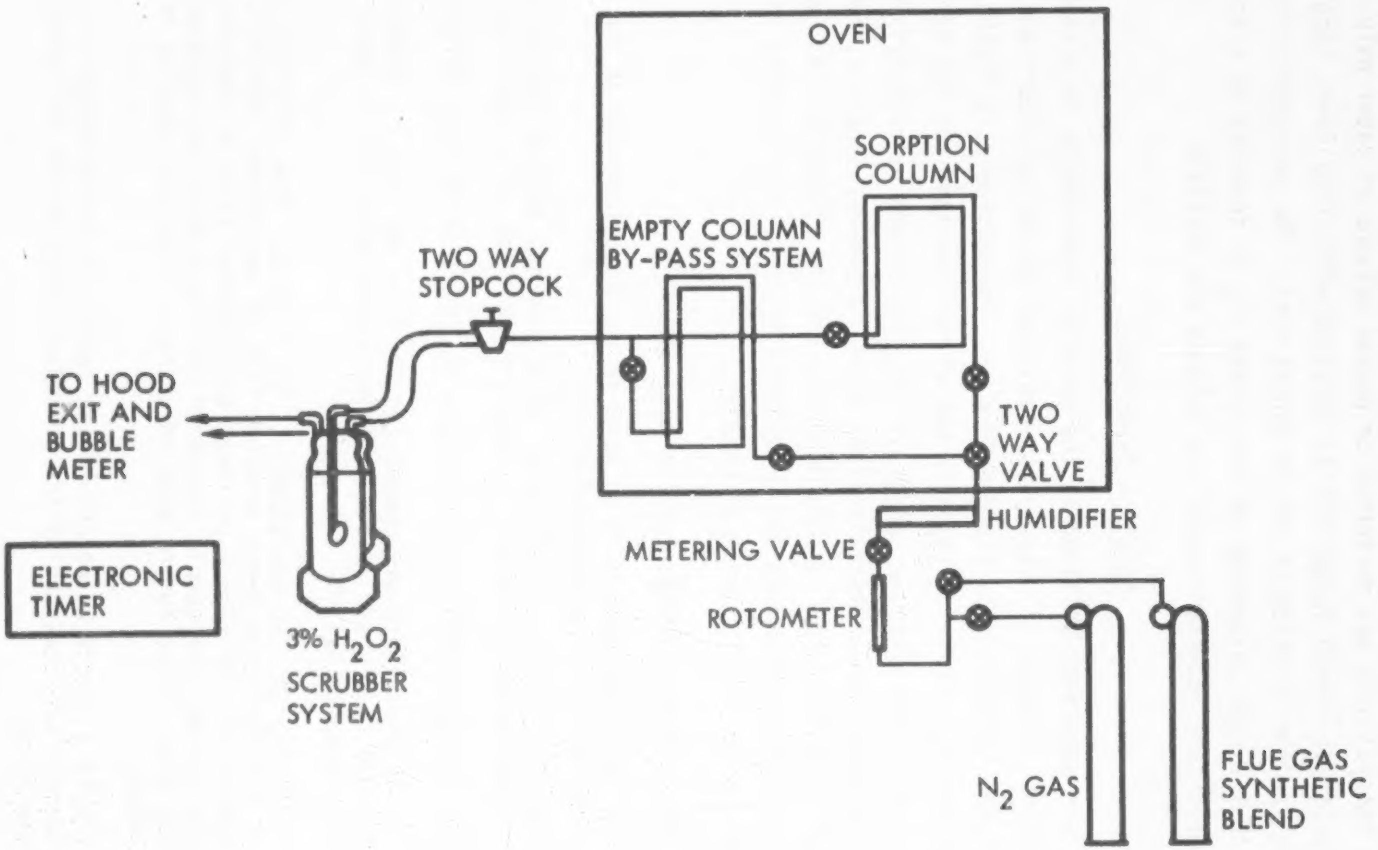
OVEN
SORPTION COLUMN
EMPTY COLUMN BY-PASS SYSTEM
TWO WAY STOPCOCK
TWO WAY VALVE
HUMIDIFIER
METERING VALVE
ROTOMETER
N_2 GAS
FLUE GAS SYNTHETIC BLEND
TO HOOD EXIT AND BUBBLE METER
ELECTRONIC TIMER
3% H_2O_2 SCRUBBER SYSTEM

FIGURE 7. Sorption Test Apparatus

The samples obtained in Step f. above are analyzed by the following procedure:

a. The solutions are rinsed from the scrubbers into 250 cc beakers.

b. The solutions are reduced in volume from 150 cc to approximately 5 cc by boiling.

c. 4 cc of acetone and 3 drops of Sulfonazo III indicator solution is added to the solution.

d. The resulting solution is titrated with 0.01 N $Ba(ClO_4)_2$ solution to a blue end point.

e. Calculations are as follows:

$$\text{A.} \quad (\text{mg } SO_2 \text{ recovered}) = T \times N \times 64.0$$

where:

T = $Ba(ClO_4)_2$ titer (ml)

N = Normality of $Ba(ClO_4)_2$ solution.

$$\text{B.} \qquad \% \text{ Vol } SO_2 = \frac{\frac{A}{2.927}}{\frac{A}{2.927} + C}$$

where:

A = mg SO_2 recovered

C = Volume of gas passed through the system in the one-minute period

2.927 = SO_2 gas density mg/cc.

Desorption Experiments

The desorption apparatus is presented schematically in Figure 8. The system consists of two cylinders containing N_2 gas and 30% SO_2 - N_2 gas blend respectively, an oven capable of 400°C temperature, desorption column systems, a two stopcock, dual pyrex glass scrubbers, a marionette bottle equipped with a two-way stopcock and a graduated cylinder. The desorption experiments were conducted by the following procedure:

a. The oven was allowed to reach thermal equilibrium at approximately 102°C.

b. A flow of 30% SO_2 gas blend was initiated through the column and maintained at 25 column volumes per hour for 90 minutes. Saturation is assumed.

c. The column is reduced to ambient temperature and 200 cc of gas displaced with N_2 utilizing the scrubber system. A sample is taken to determine the percentage of ellage swept by this procedure.

d. The column is isolated and the oven allowed to thermally equilibrate at desorption temperature.

e. When the column is at temperature, the valve connecting column and scrubber system is opened and the gas allowed to expand through the scrubber.

f. A slow N_2 gas flow is initiated and 15 samples are obtained at one-minute intervals as described in this sorption procedure. The volume of N_2 passed per minute is recorded by reading the graduated cylinders at the completion of each one-minute sample period.

g. The samples are analyzed and SO_2 recovered calculated by the methods given for the sorption procedure.

The results for the sorption runs are given in Figures 3 and 4. The results are reported in % vol/vol SO_2 as a function of time.

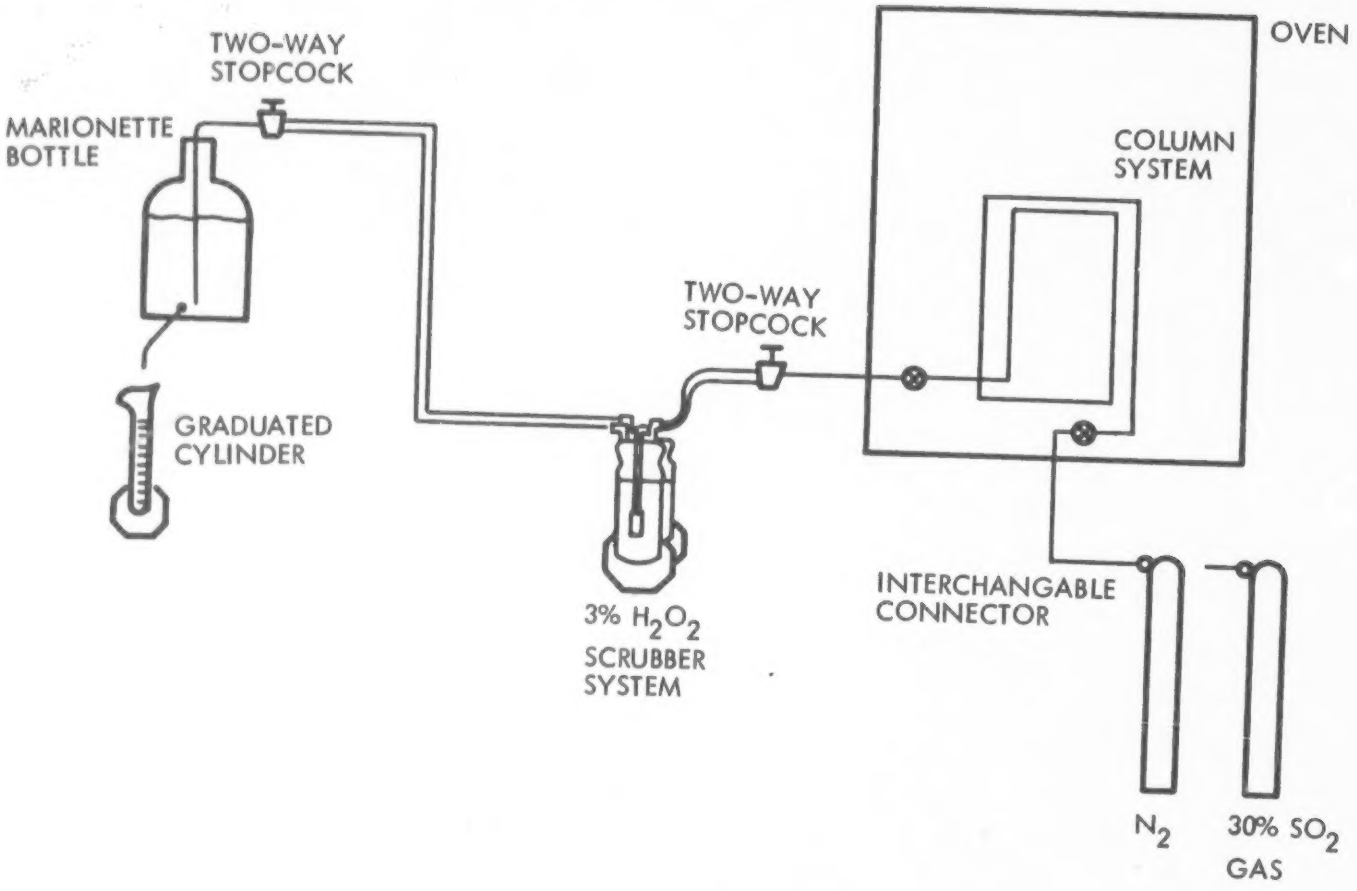
OVEN
COLUMN SYSTEM
MARIONETTE BOTTLE
TWO-WAY STOPCOCK
TWO-WAY STOPCOCK
GRADUATED CYLINDER
3% H_2O_2 SCRUBBER SYSTEM
INTERCHANGABLE CONNECTOR
N_2
30% SO_2 GAS

FIGURE 8. DESORPTION TEST APPARATUS

DIVISION III

PHASE III

Preliminary Engineering Designs and Cost Estimates

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1.0 INTRODUCTION AND SUMMARY

This report division presents the Phase III activities for preliminary engineering designs and cost estimates for control of sulfur dioxide emissions. The National Air Pollution Control Administration requested preliminary engineering designs and estimates of investment and operating costs for utilizing an organic sorbent for control of the four sulfur dioxide contamination sources shown below:

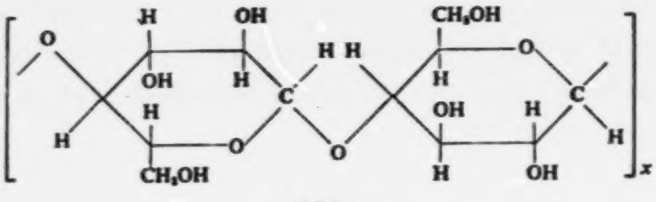
Description	Flue Gas Rate MMSCFM	Inlet SO_2 Conc. VPPM	Outlet SO_2 Conc. VPPM
Large New Power Plant	2.5	3×10^3	150
Large Existing Power Plant	2.5	3×10^3	150
Small Existing Power Plant	.5	3×10^3	300
New Smelter	.02	5×10^4	5×10^3

As a result of work performed in Phases I and II of this study, it was shown that the most promising class of organic solid for removal of SO_2 from flue gases is cellulose containing materials such as wood, cotton, and newsprint. In particular, it was found that newsprint sorbs sulfur dioxide from synthetic flue gas streams at operating temperatures, and has the best balance of physical properties, chemical properties, availability and cost. The process for utilizing newsprint which was selected, employs a moving-bed of shredded paper as a sorbent of sulfur dioxide from flue gas streams. The sulfur dioxide is subsequently removed from the paper by thermal desorption for use as a feed stream in sulfuric acid manufacture.

The following sections present the approaches, methods and results of the process design and economic analyses performed on the sulfur dioxide removal and recovery process for each of the four design cases. Section 2 presents a discussion of the chemistry pertaining to the sorption of sulfur dioxide by cellulosics. The reduction of previously conducted experimental work into process design parameters is discussed in Section 3. Section 4 and 5 present the process designs and economic evaluations of the four design cases. Process safety is discussed in Section 6. Section 7 presents the conclusions based on the results of the process design and economic evaluations and also recommendations related to the application of the sulfur dioxide recovery process. Patent applications resulting from the study are described in Section 8, References in Section 9, and Section 10 is an Appendix.

2.0 DISCUSSION OF CHEMISTRY

Waste paper (newsprint) selected as the SO_2 sorbent for the Phase III engineering analysis contains roughly 75% cellulose, which is a ladder polymer with a large number of alcohol and ether functional groups:



Cellulose

Because of the double strand chemical backbone, construction, cellulosics generally do not begin rapid thermal decomposition below 500-600°F, and are fairly stable at flue gas stack temperatures. Cellulosics also have molecular weights as high as 400 million and therefore possess excellent mechanical properties. Thus, cellulose containing materials are strong and flexible and resistant to loss of mechanical properties under repeated stress-strain conditions. This property is important in reducing mechanical losses of sorbent during use. The regenerable sorption of SO_2 by cellulose probably occurs by a combination of physical sorption and chemisorption mechanisms as charge transfer interactions and insertion reactions.

CHARGE TRANSFER

$$\text{CELLULOSE} + n\ SO_2 \rightleftharpoons \text{CELLULOSE} \cdot (SO_2)_n$$

$$K_{equil} = \frac{\left[\text{CELLULOSE} \cdot (SO_2)_n\right]}{\left[\text{CELLULOSE}\right]\left[SO_2\right]^n}$$

CHEMICAL REACTION

$$\text{CELLULOSE} - (OH)_n + nSO_2 \rightleftharpoons \text{CELLULOSE} - (OSO_2H)_n$$

$$K_{equil} = \frac{\left[\text{CELLULOSE} - (OSO_2H)_n\right]}{\left[\text{CELLULOSE} - (OH)_n\right]\left[SO_2\right]^n}$$

Charge transfer interactions are generally exothermic, and the equilibrium constant decreases as temperature increases, as does ordinary sorption. Sorption by chemical reaction could be either an endothermic or exothermic process. Thus, the overall sorption process is likely to be exothermic, and thermal desorption at higher temperatures is a possible way to regenerate the cellulose. The Phase II laboratory study indicated that newsprint has the capacity to pick up SO_2 selectively from synthetic flue gas streams in the 215°-300°F temperature range, and could be regenerated at desorption temperatures of 350°-450°F.

3.0 EXPERIMENTAL DATA REDUCTION

During Phase II of this program, a mathematical model was developed to simulate the unsteady-state sorption of SO_2 on paper in a fixed-bed sorber. In the model, the diffusion of SO_2 from the bulk of the flue gas to the solid-gas interface is the rate-determining step in the pickup of SO_2. A material balance for the SO_2 contained in a differential element of the sorber resulted in the following equation:

$$-U_o C_o \frac{\partial Y}{\partial Z} = \epsilon C_o \frac{\partial Y}{\partial t} + \rho Q \frac{\partial X}{\partial t} \qquad (1)$$

where

U_o = superficial flue gas flow rate, $\left(\frac{ft^3}{hr\text{-}ft^2 \text{ empty sorber cross section}}\right)$

C_o = SO_2 concentration in feed flue gas, (moles SO_2/ft^3)

C_G = SO_2 concentration in flue gas at position Z in the sorber and at time t, (moles SO_2/ft^3)

C_p = SO_2 concentration in the paper at position Z in the sorber and at time t, (moles SO_2/lb paper)

Q_{sat} = saturated SO_2 concentration of paper, (moles SO_2/lb paper)

Y = residual SO_2 mole ratio of the flue gas, (C_G/C_o)

X = residual SO_2 mole ratio of the paper, (C_p/Q_{sat})

ρ = density of paper, (lbs paper/ft^3 sorber)

ϵ = void fraction of column, (ft^3 actual volume/ft^3 empty sorber)

t = time, (hr).

Z = sorber length, (ft).

A material balance for the SO_2 on the solid surface results in the equation:

$$\rho \frac{\partial C_p}{\partial t} = k_g a \left(C_G - C_i\right) \qquad (2)$$

where

k_g = mass transfer coefficient, moles SO_2 on paper/(hr) (ft^2 transfer area) (moles SO_2/ft^3 flue gas).

a = area for mass transfer per unit volume, (ft^2 transfer area/ft^3 sorber).

C_i = SO_2 concentration in flue gas at gas-solid interface (moles SO_2/ft^3 flue gas).

The assumption was made that an equilibrium condition exists between the SO_2 in the gas at the solid interface and the SO_2 on the paper expressed by:

$$C_i = HC_p$$

where H = equilibrium constant.

The mathematical model was translated into a FORTRAN II computer program which uses a finite difference approach known as the "modified Euler's method" or "Henn's first method" to solve the equations. The computer program has the capability to calculate the SO_2 concentration in the flue gas and on the paper as functions of time and distance along the sorber if the following values are provided as input:

Sorber cross-section area

Sorber length

Sorber pressure

Sorber temperature

Flue gas flow rate

Concentration of SO_2 in the flue gas

Maximum allowable average SO_2 concentration in the sorber effluent gas

Saturated SO_2 concentration for paper

Weight of paper per unit sorber volume*

Void fraction of the sorber*

Mass transfer coefficient $k_g a$

SO_2 gas-solid equilibrium constant, H

Values for three of the parameters needed for modeling the SO_2 sorption: (1) the equilibrium SO_2 concentration for paper, "Qsat", (2) the mass transfer coefficient, "$k_g a$", and (3) the SO_2 gas-solid equilibrium constant, "H", were not known and therefore had to be determined experimentally. Two laboratory-scale sorption runs were carried out by passing synthetic flue gas through columns (3/8 in O.D. - 8 ft and 10 ft long) packed with paper and analyzing the effluent gas for SO_2 content. The SO_2 sorbed on the paper, determined from the difference between the SO_2 content of the gas entering and leaving the sorber, resulted in values for Qsat of 0.011 lbs SO_2/lb paper at a SO_2 feed concentration of 1.8 percent by volume and 0.006 lbs SO_2/paper at a feed concentration of 0.9 percent SO_2. The data gathered from the sorption runs were reduced into curves showing the mole ratio of the SO_2 in the column effluent to the SO_2 in the entrance stream as a function of sorption run time. The computer program described above was then used to generate similar curves in a trial and error approach to match the data. Using this technique it was found that:

$$k_g a = 350 \text{ moles } SO_2/(\text{hr})\ (\text{ft}^3 \text{ sorber})\ (\text{moles } SO_2/\text{ft}^3 \text{ flue gas})$$

---

*If the density of paper (DEN) is assumed constant, the weight of paper per unit sorber volume (ρ) and the sorber void fraction (ϵ) are related by the expression:

$$DEN = \rho/(1 - \epsilon)$$

and

$$H = 0.3 \frac{\text{moles } SO_2/ft^3 \text{ flue gas}}{\text{mole } SO_2/\text{lb paper}}$$

resulted in the best fit between the high sorption end of the experimental curves and computer generated curves.

Figures 1 and 2 show the experimental results for each of the sorption runs and also the computer generated curves that corresponded to the above $k_g a$ and H values. The $k_g a$ was determined by matching the initial portion of the experimental results since at the start of the run the equilibrium relationship would have little effect due to the SO_2-free condition of the paper. Then with the value of $k_g a$ determined, it was possible to evaluate H by matching the slope of the experimental results.

During the experimental sorption runs, an attempt was made to operate at conditions near those expected in the full-scale SO_2 sorption system. The sorption mode temperature was 215°F and the superficial gas flow rate was 0.4 SCF of flue gas/sec - ft^2 empty sorber cross section. The humidification procedure controlled the SO_2 concentration in the sorber feed gas at 1.8% and 0.9% SO_2 by volume for runs 1 and 2 respectively. It should be noted that although the initial concentrations of SO_2 were different from the two runs, the values of $k_g a$ and H determined from the data were the same for both runs. These results indicate that in the low SO_2 concentration region, the mass transfer and equilibrium coefficients are relatively independent of the SO_2 concentration, and therefore can be applied to the design cases.

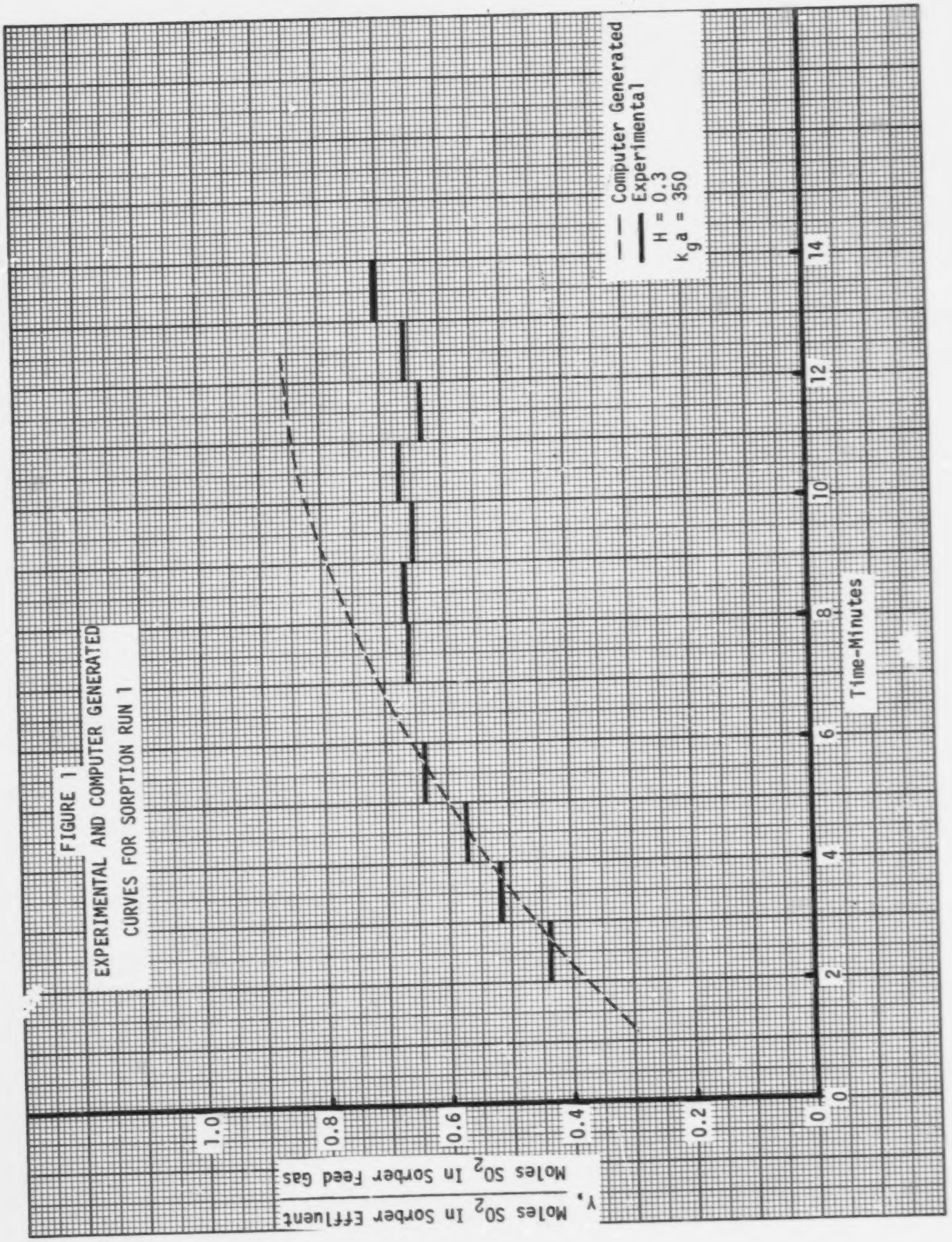


FIGURE 1

EXPERIMENTAL AND COMPUTER GENERATED CURVES FOR SORPTION RUN 1

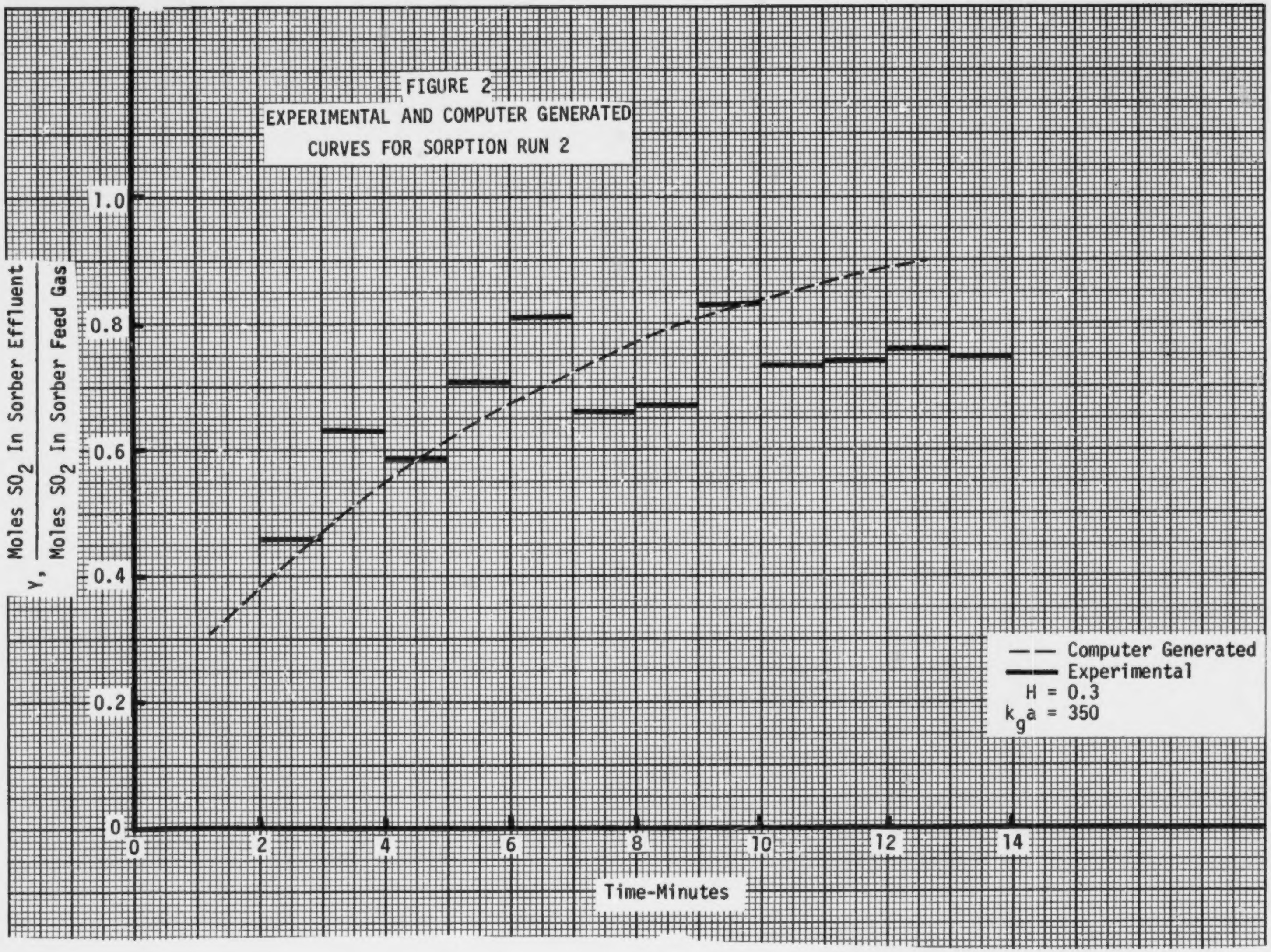


FIGURE 2

EXPERIMENTAL AND COMPUTER GENERATED CURVES FOR SORPTION RUN 2

4.0 SULFUR DIOXIDE RECOVERY PROCESS

The sulfur dioxide removal and recovery process (Figure 3) is a moving bed system which utilizes shredded waste paper as a sulfur dioxide sorbent. The process consists of essentially three steps:

- Sorption of sulfur dioxide by the paper
- Recovery of sulfur dioxide from the paper by thermal desorption
- Cooling of paper back to sorption temperature

The end-product of the recovery process is a 9 percent sulfur dioxide stream which may be further processed to sulfuric acid or elemental sulfur.

4.1 SORPTION PROCESS DESCRIPTION

Flue gas containing sulfur dioxide enters the moving-bed sorber, where shredded paper packed in baskets on rails is moving slowly in the opposite direction (Figure 4). The SO_2 in the flue gas is sorbed on the paper, and the baskets are then moved to the thermal desorption station, where the SO_2 is released from the paper by passing through bursts of hot flue gas at 450°F, heating up only the surface and not the bulk of the paper.

The desorption gas is recirculated until its SO_2 concentration reaches 9 percent and then a fraction of the stream is drawn off (and sent to either a sulfuric acid plant or a unit for elemental sulfur recovery) while an equivalent amount of hot flue gas is added as make-up. The SO_2 concentration in the draw-off stream is maintained at 9 percent, the level showing the best economic return in the manufacture of sulfuric acid. The desorption gas stream is reheated to 450°F in each cycle by heat exchanging with hot flue gas from the power plant or smelter source. After removal of the SO_2, the paper carrier baskets are moved to the other end of the sorber system, and then cooled to the sorption temperature (215°F) with air before they reenter the sorption chamber. Also in the air-cooled station, fresh paper is added to the baskets to replace the amount that has undergone structural degradation. The spent paper is sent to the burner as a fuel source. The SO_2 free flue gas after exiting from the moving bed sorber is sent to the stacks.

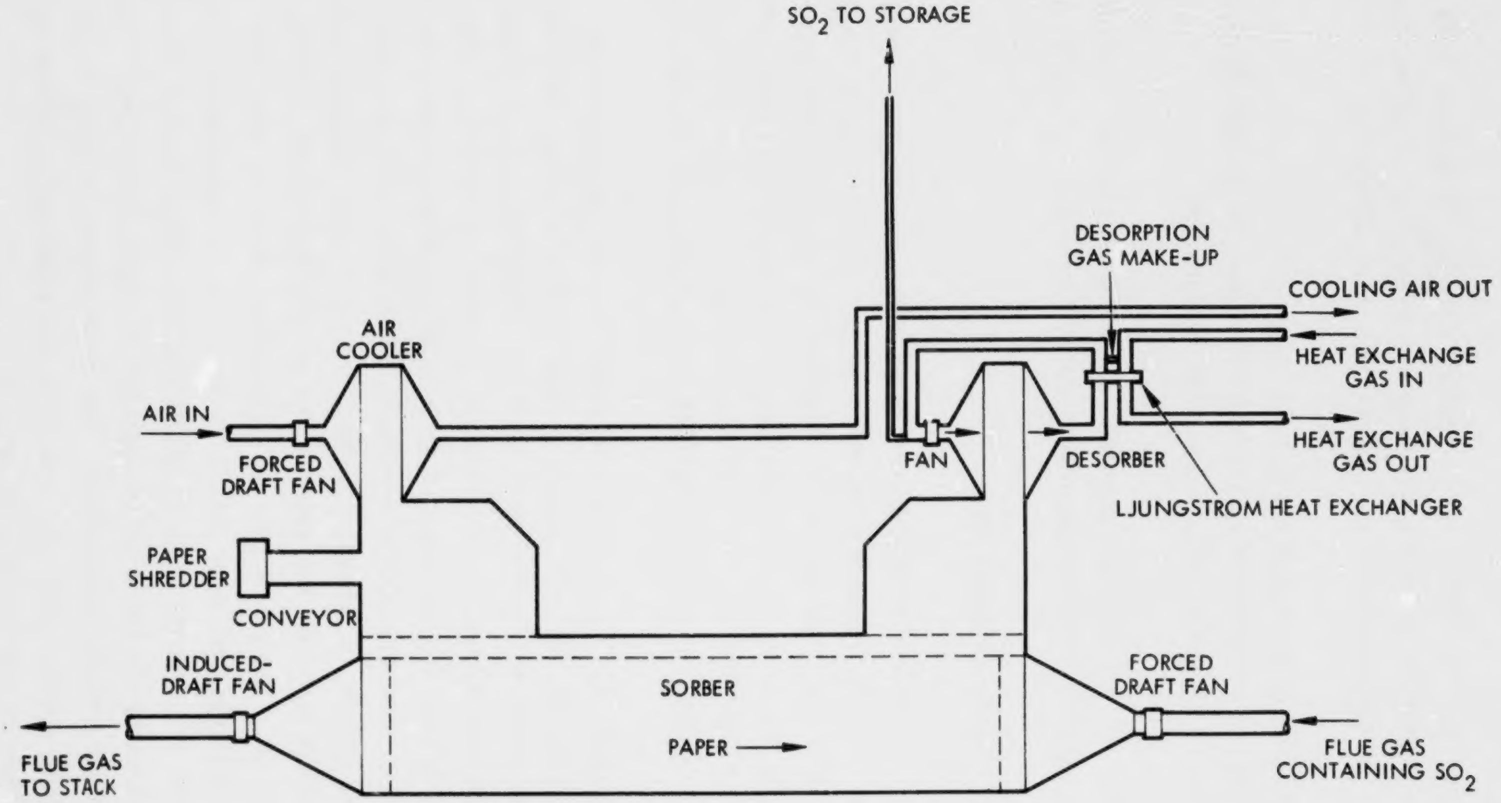

SO_2 TO STORAGE
DESORPTION GAS MAKE-UP
COOLING AIR OUT
AIR COOLER
AIR IN
HEAT EXCHANGE GAS IN
FORCED DRAFT FAN
FAN
DESORBER
HEAT EXCHANGE GAS OUT
LJUNGSTROM HEAT EXCHANGER
PAPER SHREDDER
CONVEYOR
INDUCED-DRAFT FAN
SORBER
FORCED DRAFT FAN
PAPER
FLUE GAS TO STACK
FLUE GAS CONTAINING SO_2

Figure 3. Sulfur Dioxide Removal and Recovery Process

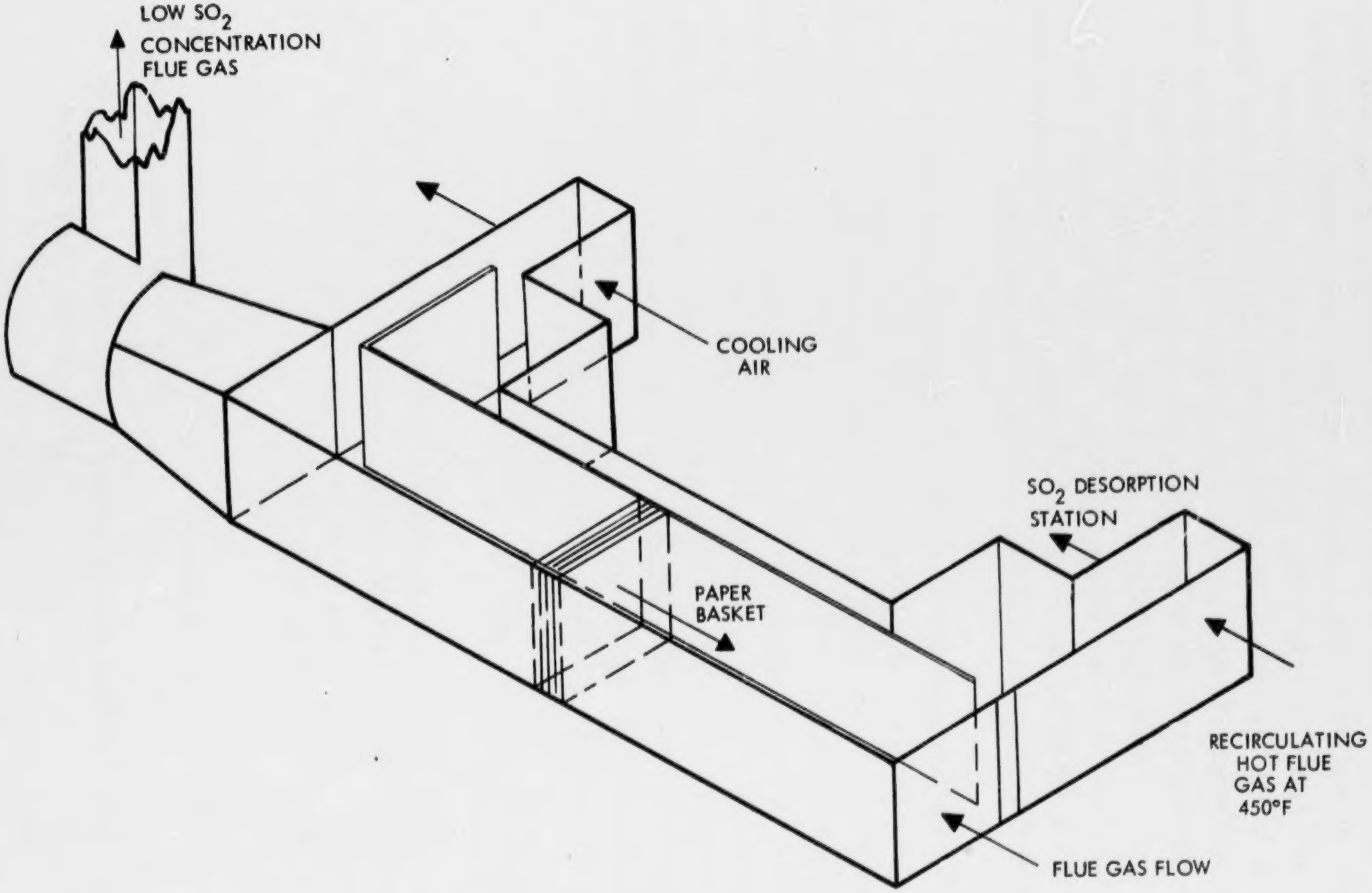

LOW SO_2 CONCENTRATION FLUE GAS
COOLING AIR
SO_2 DESORPTION STATION
PAPER BASKET
RECIRCULATING HOT FLUE GAS AT 450°F
FLUE GAS FLOW

Figure 4. Moving-Bed Sorber System

The sorber system designed for the power plant and smelter cases is a horizontal conduit with a rectangular cross section. During sorption, a network of individual "paper baskets" traveling on a railed transporter system move at a slow rate in the opposite direction of the flue gas Figure 5). As the baskets reach the entering flue gas end of the sorber, each is accelerated forward a short distance and then pulled sideways into the desorption station where the baskets are subjected to short bursts of hot flue gas. Following desorption, the baskets are pivoted, forwarded to the opposite end of the sorber, again pivoted, and pulled into the air-cool stations where the "paper basket" is cooled to the sorber temperature. Completing the cycle, the basket is sent back into the sorber.

A fixed-bed mode of operation for the paper sorber-desorber was considered but extensive engineering design problems were encountered. The fixed-bed mode with its relative ease of operation could prove advantageous for a case in which the flue gas rates are low. But, for the power plant and smelter cases considered, the heat and time requirements were evaluated to be economically unfavorable compared to a moving bed operation. In a similar manner, a fluidized bed operation might prove feasible for a case in which the pressure drop through the bed could be economically overcome, but this mode did not appear practical for the four cases considered. A discussion of a fixed-bed design can be found in Appendix B .

4.2 PROCESS MATHEMATICAL MODEL

A mathematical model was developed to simulate the operation of a countercurrent moving-bed sorption system. In the sorption step, SO_2 is transferred from the gas phase to the paper surface in a steady-state operation. With reference to Figure 6, let

$$G = \text{superficial flue gas mass velocity} \left(\frac{\text{lbs flue gas}}{\text{hr-ft}^2 \text{ empty cross section}} \right)$$

$$S = \text{superficial paper mass velocity} \left(\frac{\text{lbs paper}}{\text{hr-ft}^2 \text{ empty cross section}} \right)$$

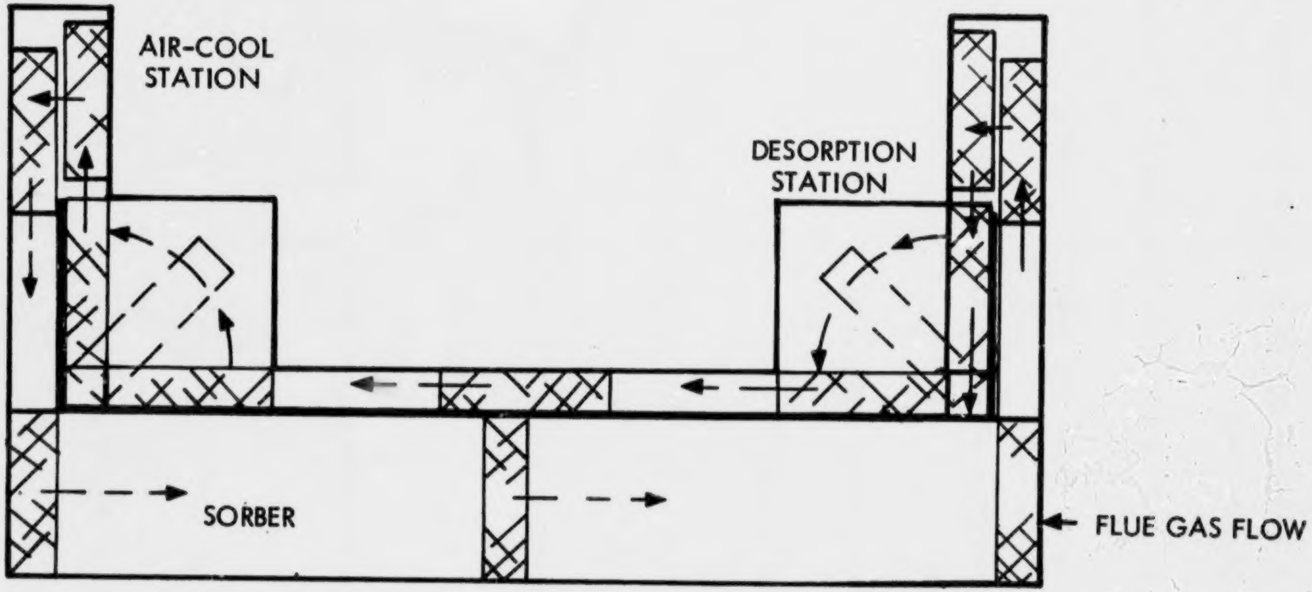

AIR-COOL
STATION
DESORPTION
STATION
SORBER
FLUE GAS FLOW

Figure 5. Progress of Paper Basket (Top View)

ω_G = mass fraction of SO_2 in the flue gas at position Z (lbs SO_2/lb flue gas)

ω_s = mass fraction of SO_2 on the paper at position Z (lbs SO_2/lb paper)

ρ_G = density of flue gas, (lbs flue gas/ft^3 flue gas)

ρ_s = density of paper (lbs paper/ft^3 paper)

ε = void fraction of sorber (ft^3 actual volume/ft^3 empty sorber volume)

Z = distance along sorber (ft)

L = sorber length (ft)

ω^*_{sG} = equilibrium SO_2 mass fraction at the gas-solid interface (lbs SO_2/lb flue gas)

H = equilibrium constant $\left(\dfrac{\text{lbs } SO_2/\text{ft}^3 \text{ flue gas}}{\text{lbs } SO_2/\text{lb paper}}\right)$

$$\left[\omega^*_{sG} = \frac{H}{\rho_G}\,\omega_s\right]$$

k_ga = mass transfer coefficient, $\dfrac{\text{lbs } SO_2}{\text{hr-ft}^3 \text{ sorber} \dfrac{(\text{lbs } SO_2)}{\text{ft}^3 \text{ flue gas}}}$

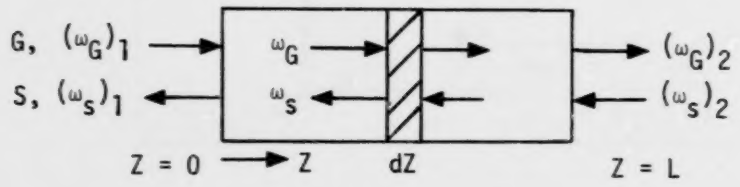


FIGURE 6. MOVING-BED SORBER

It was assumed that G, S, ρ_G, ρ_s, ε, $k_g a$ and H remain constant over the operating range. Composition gradients of SO_2 within the interior of the paper were neglected.

The boundary conditions of the model are expressed as

$$\omega_G = \left(\omega_G\right)_1 \quad \text{at } Z = 0 \qquad \omega_G = \left(\omega_G\right)_2 \quad \text{at } Z = L$$
$$\omega_s = \left(\omega_s\right)_1 \qquad\qquad\qquad \omega_s = \left(\omega_s\right)_2$$

The overall mass balance for the sorber results in

$$G\left[\left(\omega_G\right)_1 - \left(\omega_G\right)_2\right] = S\left[\left(\omega_s\right)_1 - \left(\omega_s\right)_2\right] \tag{3}$$

and a mass balance for a differential element of the sorber is

$$d\left(G\omega_G\right) = d\left(S\omega_s\right) = -k_g a\rho_G\left(\omega_G - \omega^*_{sG}\right)dZ \tag{4}$$

Equation (4.2) was derived assuming that the diffusion of SO_2 from the bulk of the flue gas to the solid-gas interface is the rate controlling step in the sorption of SO_2 onto paper.

The assumption was also made that an equilibrium condition exists between the SO_2 at the solid-gas interface and the SO_2 on the paper, and that this condition can be expressed by the relationship

$$\omega^*_{sG} = \frac{H}{\rho_G}\,\omega_s$$

Substituting in (4.2) yields

$$G d\omega_G = -\,k_g a\rho_G\left(\omega_G - \frac{H}{\rho_G}\,\omega_s\right)dZ \tag{5}$$

Now a mass balance from some position Z in the sorber to the end of the sorber gives

$$G\left[\omega_G - \left(\omega_G\right)_2\right] = S\left[\omega_s - \left(\omega_s\right)_2\right]$$

or rearranging

$$\omega_s = \frac{G}{S}\left[\omega_G - \left(\omega_G\right)_2\right] + \left(\omega_s\right)_2 \tag{6}$$

Substituting (4.4) into (4.3) and integrating

$$\int_0^L dZ = \int_{(\omega_G)_2}^{(\omega_G)_1} \frac{d\omega_G}{\left[\frac{k_g a\rho_G}{G}\left(1 - \frac{HG}{\rho_G S}\right)\right]\omega_G + \frac{k_g aH}{G}\left[\frac{G(\omega_G)_2}{S} - (\omega_s)_2\right]}$$

results in the following relationship

$$L = \frac{1}{A}\,\ell n\left[\frac{A(\omega_G)_1 + B}{A(\omega_G)_2 + B}\right] \tag{7}$$

where

$$A = \frac{k_g a\rho_G}{G}\left[1 - \frac{HG}{\rho_G S}\right]$$

$$B = \frac{k_g aH}{G}\left[\frac{G(\omega_G)_2}{S} - (\omega_s)_2\right].$$

In addition, integrating over some distance Z of the sorber gives

$$Z = \frac{1}{A}\,\ell n\left[\frac{A\ (\omega_G)_1 + B}{A\ \omega_G + B}\right]$$

or

$$\omega_G = \left[(\omega_G)_1 + \frac{B}{A}\right]e^{-AZ} - \frac{B}{A} \tag{8}$$

Substituting (4.6) into (4.4) yields

$$\omega_s = \left[(\omega_G)_1 + \frac{B}{A}\right] \frac{G}{S} e^{-AZ} - \frac{G}{S}\left[(\omega_G)_2 + \frac{B}{A}\right] + (\omega_s)_2 \qquad (9)$$

Equations (4.5), (4.6), and (4.7), along with the stated assumptions and boundary conditions define the mathematical model for predicting the steady-state operation of the moving bed sorber.

5.0 PROCESS ENGINEERING AND ECONOMIC ANALYSIS

Process engineering, design and economic evaluation of the sulfur dioxide recovery process as applied to four sulfur dioxide emission sources was conducted. The four cases considered were:

CASE	DESCRIPTION	FLUE GAS RATE (MMSCFM)	INLET SO_2 (% vol)	OUTLET SO_2 (% vol)
1	Large new power plant	2.5	0.3	0.015
2	Large existing power plant	2.5	0.3	0.015
3	Small existing power plant	0.5	0.3	0.03
4	New smelter	0.02	5.0	0.5

In the engineering analysis the following flue gas compositions were considered typical:

Component	Power Plant Cases % by Volume	Smelter Case % by Volume
N_2	74.9	70.3
CO_2	14.7	1.9
H_2O	7.25	11.7
O_2	2.8	11.1
SO_2	0.3	5.0
NO_x	0.05	
Fly Ash	0.2 (weight)	

A process design and the estimates of investment and operating costs for each case follow.

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5.1 LARGE NEW POWER PLANT CASE

The sulfur dioxide recovery process for the large new power plant case is designed to remove and recover 95 percent of the sulfur dioxide present in a flue gas stream flowing at a rate of 2.5 MMSCFM (approximately 573 MM lbs of sulfur dioxide per year). This flue gas rate would correspond to a power plant generating approximately 1100 Megawatts of electrical power while consuming 480 tons of coal per hour as fuel.* The power plant is estimated to occupy a site of approximately 400 acres. The sulfur dioxide recovery process will require approximately 20 acres on the power plant site (Figure 7).

5.1.1 Process Design Analysis

The sulfur dioxide recovery process is a moving bed sorber/thermal desorber system as described in Section 4. The process flow diagram and the results of the mass and heat balance, for the large new power plant case are presented in Figure 8. As shown in the figure, the power plant flue gas stream after passing through the air preheater and the dust collector (Stream 1) is sent to the sorber. Here 95 percent of the sulfur dioxide in the flue gas is sorbed onto paper held in baskets and moving at a slow rate counter current to the flue gas flow. The flue gas exiting the sorber (Stream 2) is monitored for sulfur dioxide content by an infrared spectrophotometer and is then sent to the stacks.

The baskets containing the paper, as they reach the flue gas entrance end of the sorber, are pulled into the desorber where bursts of reducing gas at 450°F (Stream 6) pass through the paper and thermally desorb the sulfur dioxide. The baskets containing the paper are 10 feet in length so that the hot gas heats only the paper surfaces. The hot desorption gas stream is held at a 9 percent sulfur dioxide concentration by continuously withdrawing a portion for sulfuric acid manufacture (Stream 3) and adding hot flue gas (Stream 10). The temperature of the desorption gas stream is maintained by heat exchanging with approximately 20 percent of the flue gas leaving the economizer (Stream 8).

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* The power plant size is based on the assumption that the combustion of one ton of coal with 20% excess air produces 0.311 MMSCF of flue gas and generates 2300 KWH of electrical power (Reference).

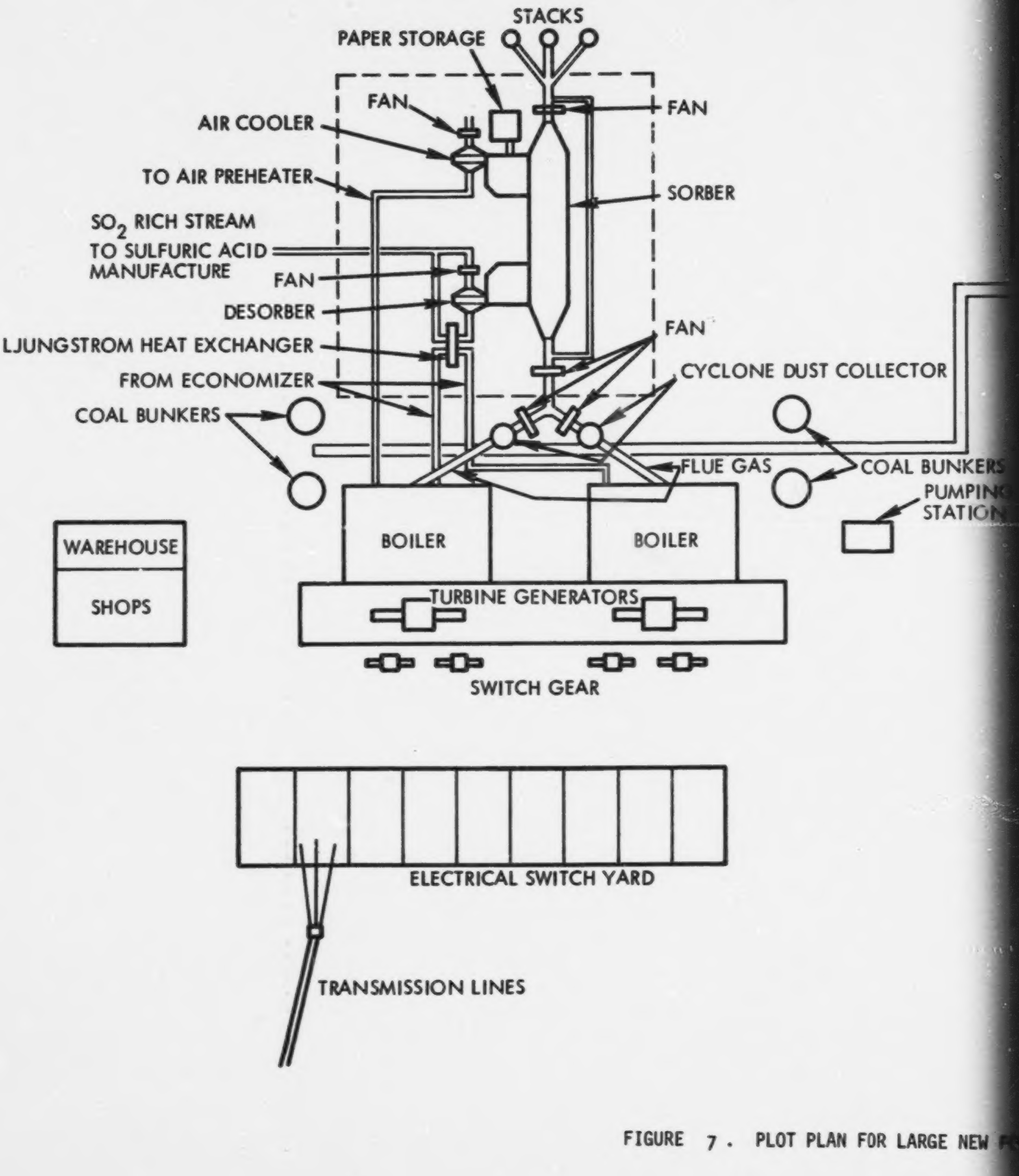
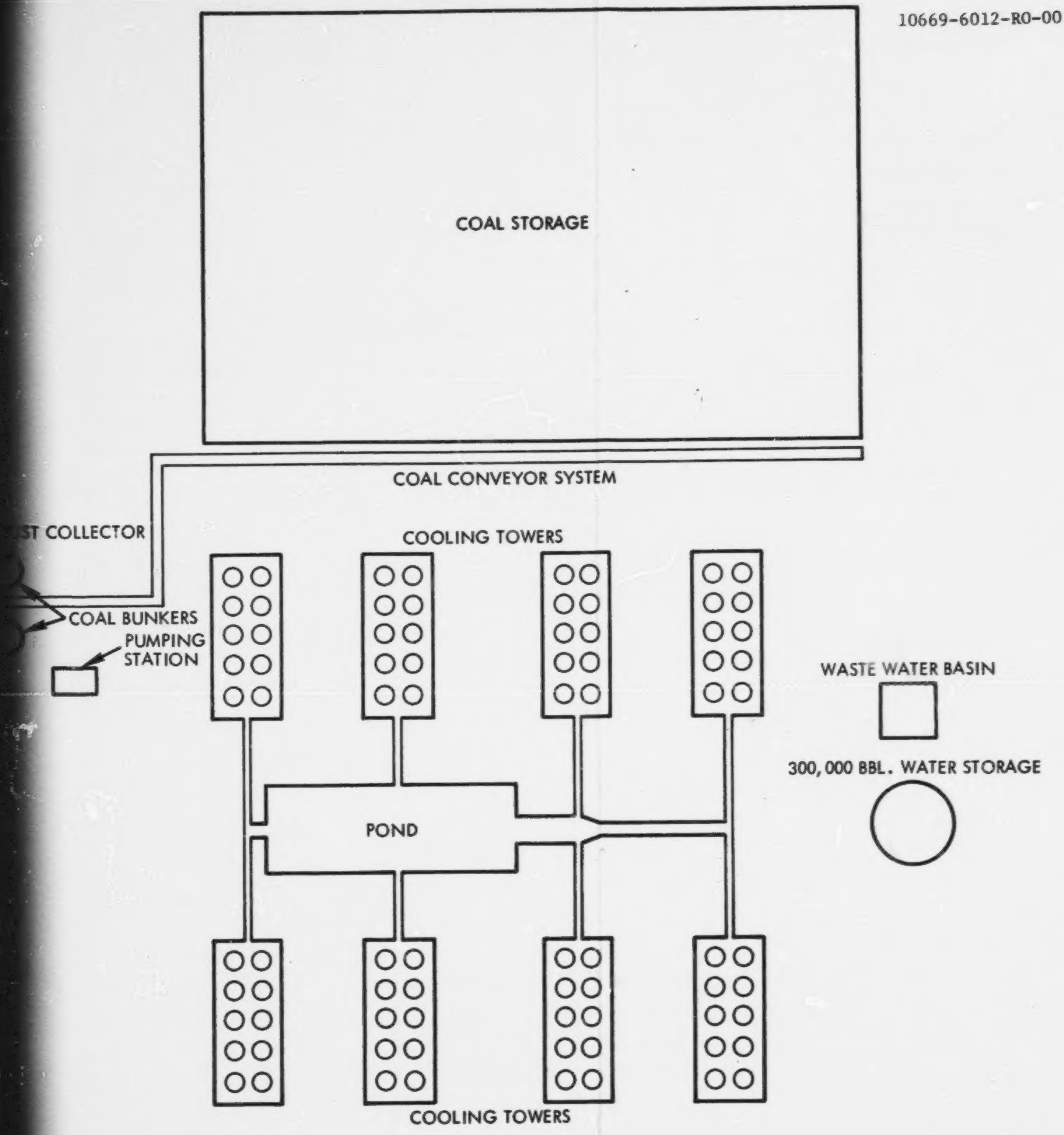
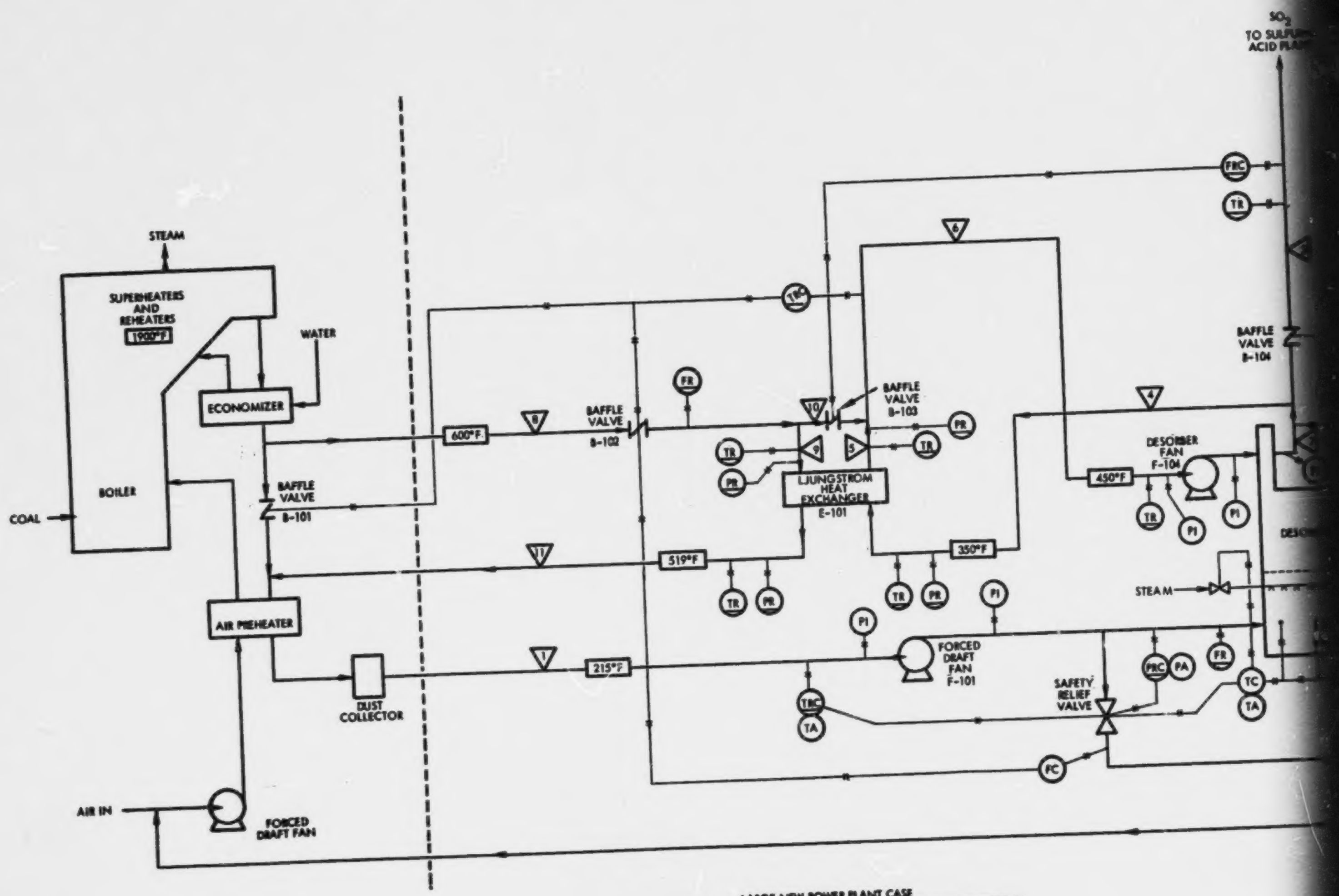

STACKS
PAPER STORAGE
FAN
AIR COOLER
TO AIR PREHEATER
SO_2 RICH STREAM
TO SULFURIC ACID
MANUFACTURE
FAN
DESORBER
LJUNGSTROM HEAT EXCHANGER
FROM ECONOMIZER
COAL BUNKERS
FAN
SORBER
FAN
CYCLONE DUST COLLECTOR
FLUE GAS
COAL BUNKERS
PUMPIN
STATION
WAREHOUSE
SHOPS
BOILER
BOILER
TURBINE GENERATORS
SWITCH GEAR
ELECTRICAL SWITCH YARD
TRANSMISSION LINES

FIGURE 7. PLOT PLAN FOR LARGE NEW


COAL STORAGE
COAL CONVEYOR SYSTEM
ST COLLECTOR
COOLING TOWERS
COAL BUNKERS
PUMPING STATION
WASTE WATER BASIN
300,000 BBL. WATER STORAGE
POND
COOLING TOWERS

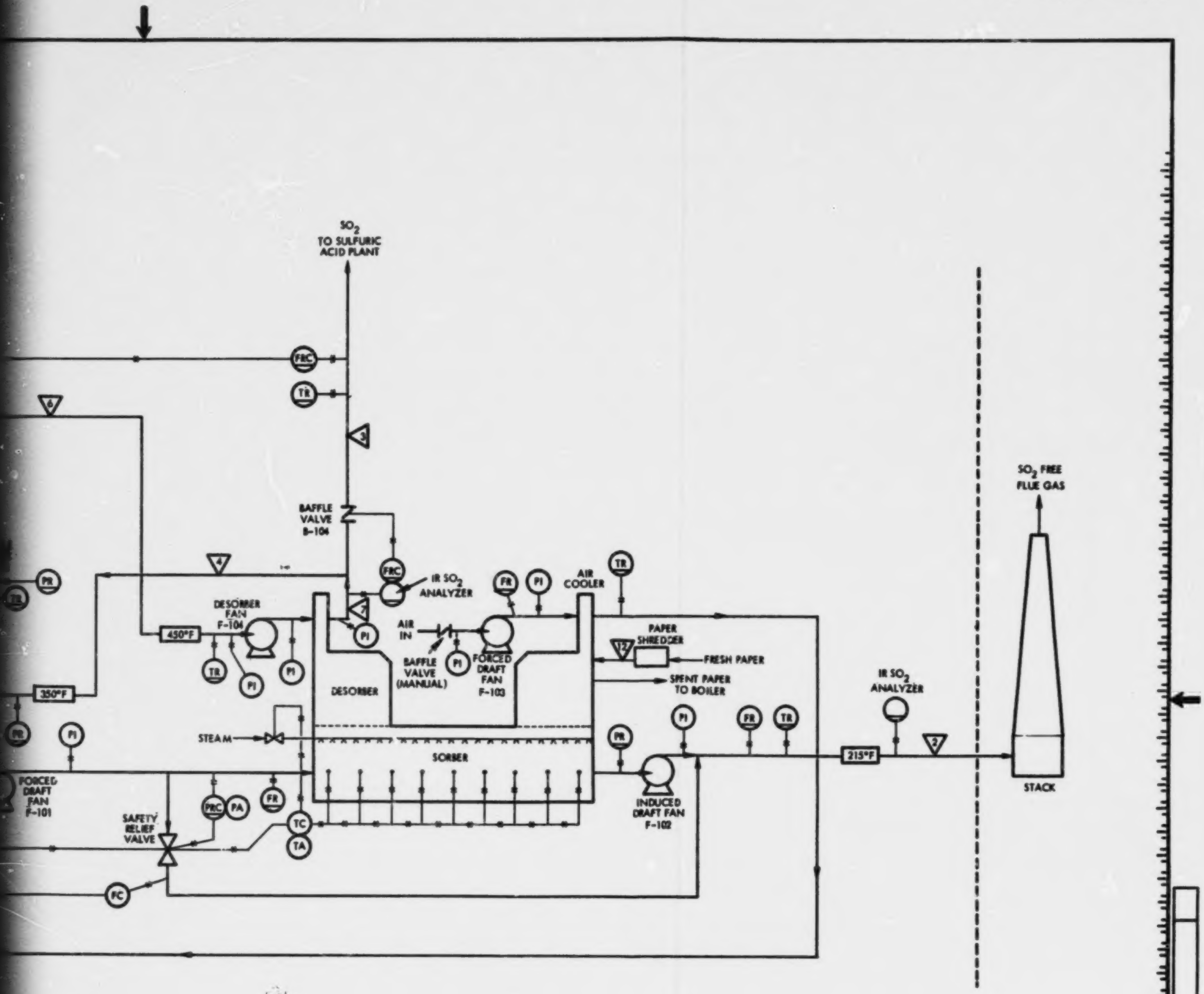
APPROXIMATE SCALE: 1 INCH = 400 FEET

LAN FOR LARGE NEW POWER PLANT WITH SO_2 RECOVERY SYSTEM


STEAM
SUPERHEATERS AND REHEATERS
1900°F
WATER
ECONOMIZER
BOILER
COAL
BAFFLE VALVE B-101
AIR PREHEATER
DUST COLLECTOR
AIR IN
FORCED DRAFT FAN
600°F
8
BAFFLE VALVE B-102
FR
TRC
10
BAFFLE VALVE B-103
PR
TR
9
5
TR
PR
LJUNGSTROM HEAT EXCHANGER E-101
6
11
519°F
TR
PR
350°F
TR
PR
1
215°F
PI
PI
FORCED DRAFT FAN F-101
TRC
TA
SAFETY RELIEF VALVE
PRC
PA
FR
TC
TA
FC
FRC
TR
SO2 TO SULFURIC ACID PLANT
BAFFLE VALVE B-104
4
450°F
DESORBER FAN F-104
TR
PI
PI
DESORBER
STEAM

LARGE NEW POWER PLANT CASE

STREAM NO.	MOLES/HR OF SPECIES					TONS/HR PAPER	MM BTU/HR H - H 298°F
	SO_2	N_2	CO_2	H_2O	O_2		
1	1,156	288,635	56,648	27,938	10,790		422.491
2	58	288,635	56,648	27,938	10,790		420.957
3	1,131	8,587	1,685	831	321		27.996
4	9,851	74,875	14,695	7,247	2,797		344.091
5	9,870	76,620	15,626	7,707	2,975		347.012
6	9,885	83,204	16,329	8,053	3,109		366.936
7	10,982	83,204	16,329	8,053	3,109		271.341
8	386	96,259	18,891	9,316	3,597		536.850
9	371	92,687	18,190	8,971	3,464		516.926
10	15	3,573	701	346	134		19.922
11	352	87,943	17,259	8,512	3,286		414.005
12	—	—	—	—	—	36	—


SO_2 TO SULFURIC ACID PLANT
FRC
TR
3
6
4
7
BAFFLE VALVE B-104
FRC
IR SO_2 ANALYZER
FR
PI
AIR COOLER
TR
PR
TR
DESORBER FAN F-104
450°F
TR
PI
PI
PI
AIR IN
BAFFLE VALVE (MANUAL)
PI
FORCED DRAFT FAN F-103
PAPER SHREDDER
12
FRESH PAPER
SPENT PAPER TO BOILER
DESORBER
350°F
PR
PI
STEAM
SORBER
FORCED DRAFT FAN F-101
SAFETY RELIEF VALVE
PRC
PA
FR
TC
TA
FC
PR
INDUCED DRAFT FAN F-102
PI
FR
TR
215°F
IR SO_2 ANALYZER
2
SO_2 FREE FLUE GAS
STACK

MM BTU/HR H - H 298°F
422.491
420.957
27.996
344.091
347.012
366.936
271.341
536.850
516.926
19.932
414.005
—

KEY FOR INSTRUMENTATION

○	MOUNTED LOCALLY
⊖	MOUNTED IN CONTROL ROOM
FR	FLOW RECORDER
FRC	FLOW RECORDER CONTROLLER
PA	PRESSURE ALARM
PI	PRESSURE INDICATOR
PR	PRESSURE RECORDER
PRC	PRESSURE RECORDER CONTROLLER
TA	TEMPERATURE ALARM
TC	TEMPERATURE CONTROLLER
TI	TEMPERATURE INDICATOR
TR	TEMPERATURE RECORDER
TRC	TEMPERATURE RECORDER CONTROLLER

TRW
SYSTEMS GROUP
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

Figure 8.

LARGE NEW
POWER PLANT FLOW DIAGRAM

SIZE D
CODE IDENT NO. 11982
SCALE
SHEET

SYSTEMS 907 REV. 4-65

The heat added to the paper during desorption is recovered in the air cooler by heat exchanging with air which is then sent to the power plant's air preheater. Fresh paper (Stream 12) is added to the baskets following the air cooling step. In the design case, the paper replacement rate is 0.1% of the weight of paper in the basket per pass through the sorber or approximately 36 tons/hr.

The moving-bed sulfur dioxide sorber was identified as the major cost item in the recovery process and therefore much of the design analysis pertains to the sorber. The physical configuration of the sorber system depends mainly on four factors: (1) the rate of sulfur dioxide sorption onto the paper, (2) the sulfur dioxide content of the paper exiting the sorber, (3) the allowable pressure drop through the sorber and (4) the rate at which the paper is moving in the sorber. The void fraction of the paper in the sorber which is also a design parameter is interrelated with the pressure drop and the paper bed velocity. The design of the sorber is based on the mathematical model presented in Section 4. The values of the mass transfer coefficient ($k_g a$ = 350 lbs SO_2/hr - ft^3 sorber - lbs SO_2/ft^3 flue gas) and the paper-sulfur dioxide equilibrium coefficient (H = 0.3 [lbs SO_2/ft^3 flue gas]/[lbs SO_2/lb paper]) determined from the fixed bed sorption experimentation as discussed in Section 3 were used as input to the model. In the design case, the paper is moving at a relatively slow velocity ($\sim$ 16 ft/min) and therefore the mass transfer mechanisms of the moving-bed are expected to approach those encountered in a fixed-bed sorber.

The mass fraction of SO_2 on the paper leaving the sorber has major importance in determining the volume of the sorber. Under the assumptions that (1) the mass fraction of sulfur dioxide in the flue gas entering the sorber, $(\omega_G)_1$, is 6.58×10^{-3} lbs SO_2/lb flue gas (0.3% SO_2 by volume), (2) 95 percent of the sulfur dioxide in the flue gas is sorbed by the paper and therefore $(\omega_G)_2$ is 3.29×10^{-4} lbs SO_2/lb flue gas, and (3) the sulfur dioxide sorbed on the paper entering the sorber is negligible, i.e., $(\omega_s)_2 = 0$, the volume of the sorber is a function of the mass fraction of sulfur dioxide on the paper exiting from the sorber $(\omega_s)_1$. Figure 9 shows the relationship between $(\omega_s)_1$ and the volume of the sorber needed for the sorption operation. The design case

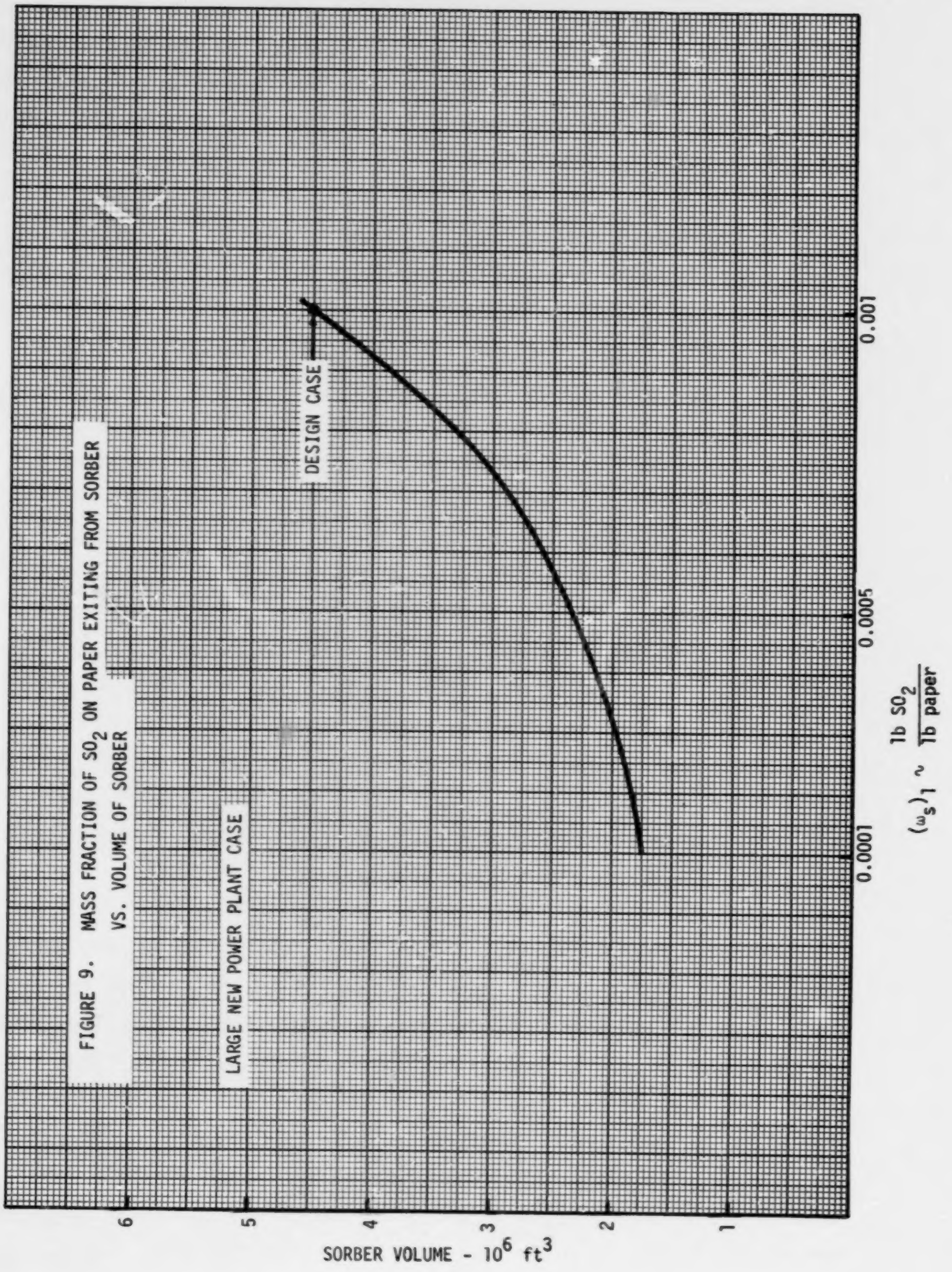


FIGURE 9. MASS FRACTION OF SO_2 ON PAPER EXITING FROM SORBER VS. VOLUME OF SORBER

value is indicated on the figure (i.e., $(\omega_s)_1$ is 0.001 lbs SO_2/lb paper and the corresponding volume of the sorber is 4.5 MM cubic feet). In the determination of the sorber volume, the assumption was made that the equilibrium coefficient, H, dictates the sulfur dioxide equilibrium capacity of the paper which for this case was calculated to be 0.0013 lbs SO_2/lb paper based on a flue gas SO_2 concentration of 0.3 volume present.

The selection of the design case sorber volume is an iterative process in which (1) the process mathematical model predicts a sorber volume, (2) the pressure drop consideration defines an allowable sorber length, and then (3) the process mathematical model is again used to determine the rate at which the paper bed is moving through the sorber. The design case is selected when the sorber volume, the pressure drop and the paper movement rate are all within reasonable limits.

The pressure drop is another parameter which must be considered in the design of the sorber. Because the paper velocity is slow in comparison to the gas flow velocity, the sorption system was considered as a fixed-bed packed column for pressure drop determination purposes. Methods of calculating the pressure drop for single-phase flow in packed beds have been developed by Leva (Reference 2), Brownell (Reference 3), and Ergun (Reference 4). Preliminary calculations indicated that the three methods would give the same order of magnitude pressure drop for the design case. The Ergun equation:

$$\frac{(-\Delta P) g_c \rho_G}{G^2} \, \frac{D_p}{L} \, \frac{\varepsilon^3}{(1 - \varepsilon)} = 150 \, \frac{(1 - \varepsilon)}{\frac{D_p G}{\mu}} + 1.75 \qquad (10)$$

where

$-\Delta P$ = pressure drop through sorber, lb_f/sq ft

g_c = conversion factor, 32.2 $(lb/lb_f)(ft/sec^2)$

ρ_G = flue gas density, lbs flue gas/ft^3

G = superficial flue gas mass velocity, $\frac{\text{lbs flue gas}}{\text{hr-ft}^2\text{ empty cross section}}$

D_p = particle diameter of an equivalent sphere, ft

L = sorber length, ft

ε = void fraction

μ = viscosity of flue gas, lbs/sec-ft

was selected for evaluating the pressure drop principally because it requires fewer assumptions.

The development of the Ergun pressure drop equation is based on the concept that as a fluid flows through the passages between solid particles, the fluid phase is repeatedly accelerated and decelerated, and experiences repeated kinetic-energy losses. In addition, the rough surfaces of the solid particles produce the usual form-drag and skin-friction losses. The Ergun equation considers the total pressure drop in a system to be a combination of the pressure losses due to form drag and those due to kinetic energy losses. The form-drag losses are expressed by a modification to an equation relating friction losses in ducts (Reference 5):

$$\frac{(-\Delta P)_f\, g_c}{L} = k_1 \frac{(1-\varepsilon)^2\, \mu G}{\varepsilon^3\, D_p^2\, \rho_G} \quad (11)$$

The kinetic-energy losses are expressed by a modification to the kinetic energy equation

$$\frac{(-\Delta P)_k\ g_c}{L} = k_2\ \frac{\rho_G \bar{v}^2}{D_c} \qquad (12)$$

where $\bar{v}$ is the average velocity of the flue gas ($G = \varepsilon\bar{v}\ \rho_G$) and D_c is an average channel diameter. If the assumption is made that in the channels under consideration, the expansions in the channel width occur at distances roughly equivalent to the channel diameter, and that the channel diameter is proportional to the particle diameter, Equation 12 can be expressed as (Reference 6):

$$\frac{(-\Delta P)_k\ g_c}{L} = k_2\ \frac{G^2}{\rho_G D_p}\ \frac{(1 - \varepsilon)}{\varepsilon^3} \qquad (13)$$

Experimental data on flow through beds of granular solids resulted in $k_1 = 150$ and $k_2 = 1.75$ (Reference 4). Using these values for k_1 and k_2, combining Equations 11 and 13 and rearranging will give the Ergun equation for pressure drop through packed beds. It should be noted that at low rates of flow through small passages, the kinetic-energy losses are small compared to the form-drag losses, but for high rates of flow through large passages the kinetic-energy losses may completely overshadow the form-drag losses.

In the design case, the allowable pressure drop through the sorber was set at 24 inches of H_2O. This pressure drop was selected because the capital cost of fans show a significant increase when the pressure head is greater than approximately 15 inches of H_2O. By employing a forced draft fan at the flue gas entrance end of the sorber and an induced draft fan at the other end, a pressure drop of 24 inches of H_2O can be overcome, and fan costs are kept to a minimum.

In determining a sorber configuration which has 4.5 MM ft^3 of volume and a pressure drop of 24 inches of H_2O, tradeoffs between the sorber length, the void fraction of the sorber, and the value assigned to D_p, the particle diameter of an equivalent sphere, become apparent. Figure 10 shows the relationship between D_p and the sorber length with the void fraction as a parameter. The indicated design case, based on a D_p of 0.5 inches and a void fraction of 0.9, has an allowable sorber length of 450 feet (and a square cross-section of 100 feet on a side). The void fraction of 0.9 corresponds to that used during the experimental work performed by TRW on packed columns of paper (Reference 7). The 0.5 inch D_p, the packing particle in terms of an equivalent sphere, seems a reasonable particle diameter if paper spheres were to be used (the Reinluft activated charcoal SO_2 removal process employs a 0.5 inch particle diameter -- Reference 8), and the fact that the design case uses shredded strips instead of solid particles should provide a conservative evaluation of the pressure drop.

In the final analysis, it must be stated that the pressure drop through a sorber packed with shredded paper does not lend itself to a direct evaluation. Mathematical models describing pressure drop for flow through packed beds indicate that by choosing the proper packing configuration, the pressure drop may remain within a tolerable range, but since the particle size, packing configuration, and pressure drop are all interrelated to the SO_2 sorption capability, only pilot plant testing can provide conclusive values for the pressure drop determination.

Other sorption parameters which apply to the design case for the large new power plant are:

- Amount of sulfur dioxide recovered is approximately 72,000 lbs/hr
- Weight of paper packing in the sorber is 15,750 tons
- Velocity of the flue gas in the sorber is 346 ft/min
- Velocity of the paper is 16.6 ft/min

Figure 11 shows the mass fraction of sulfur dioxide in the flue gas (ω_G) and the mass fraction of sulfur dioxide on the paper (ω_S) as a function of distance along the sorber.

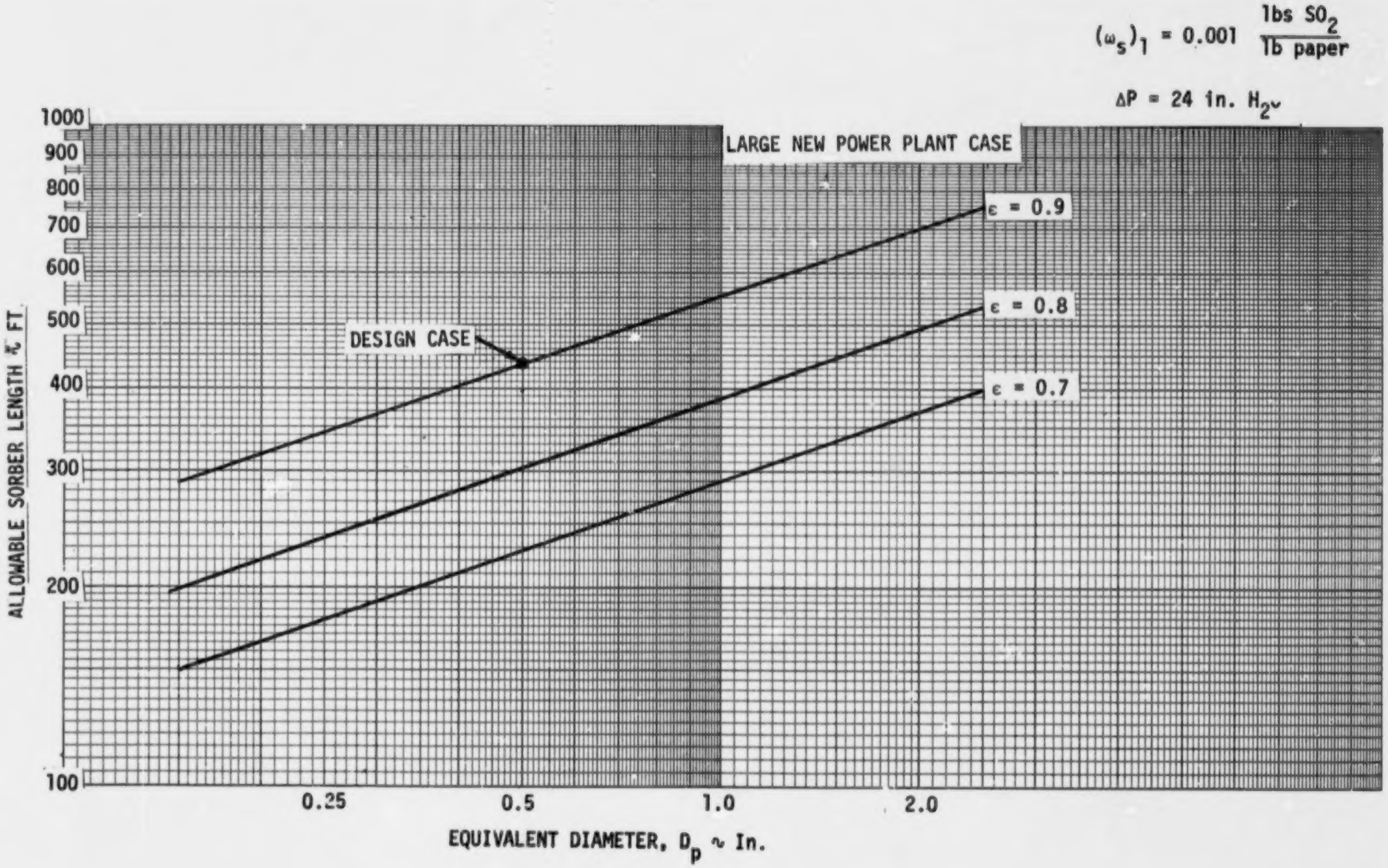


FIGURE EQUIVALENT DIAMETER OF PAPER PACKING VS. SORBER LENGTH

Figure 10. Equivalent Diameter of Paper Packing VS. Sorber Length

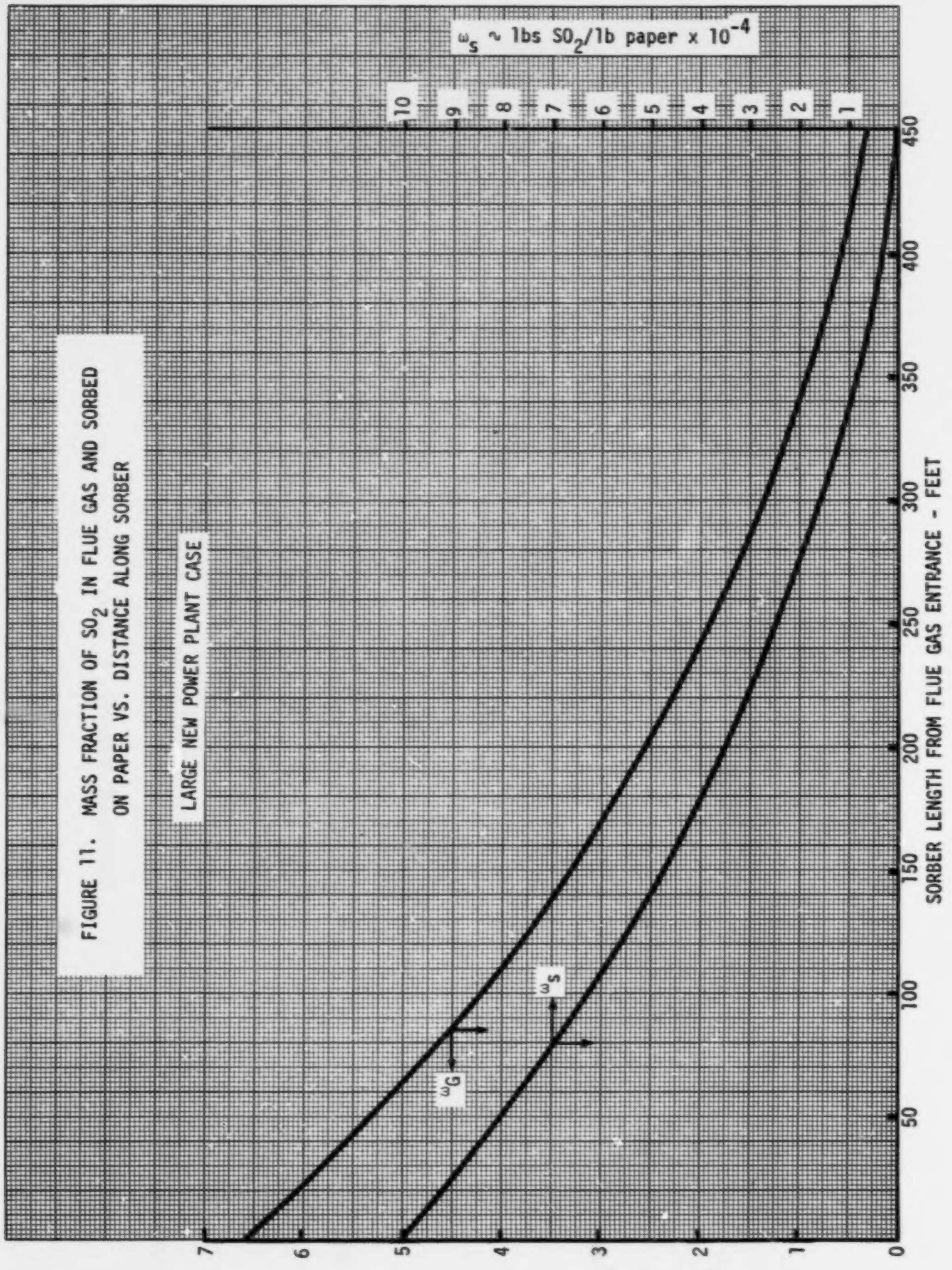


FIGURE 11. MASS FRACTION OF SO_2 IN FLUE GAS AND SORBED ON PAPER VS. DISTANCE ALONG SORBER

5.1.2 Economic Analysis

Capital and operating cost estimates were made for the process equipment required for the large new power plant case. The mass and energy balance along with the operating parameters discussed previously were used in the sizing of the process equipment. The capital and operating costs were then determined by operating price quotations from equipment manufacturers when possible and by employing cost information found in the literature.

The equipment capital and operating cost breakdown for the large new power plant case, presented in Table I and the overall process cost breakdown, presented in Table II, estimate the capital investment at \$12.8 MM and the overall process operating cost at \$147 per hour or 31 cents per ton of coal combusted. The cost considerations used in the economic analysis are presented below:

(1) The superstructure of the sorber/desorber system is constructed of reinforced concrete. The sorber section is 10^4 square feet in cross section and 450 feet in length. An additional 3.6 MM ft^3 of volume is required for the desorption and air cooling sections. The foundation concrete, poured to a thickness of 10 feet, is costed at \$55 per cubic yard of concrete installed; the wall concrete, an average of 2 feet thick, is costed at \$115 per cubic yard; and the prestressed concrete roof, also 2 feet thick, costs \$185 per cubic yard (Reference 9). A total of twelve concrete buttresses are used to add support to the concrete superstructure at a total cost of \$200K.

(2) The structured steel used in the construction of the sorber and the "paper" basket network is costed as being equivalent to that required in an 8 story office building (i.e., 11 lbs strutural steel/ft^2 floor area with an installed cost of \$350/ton - Reference 10).

TABLE I
EQUIPMENT CAPITAL AND OPERATING COST BREAKDOWN
LARGE NEW POWER PLANT CASE

	Installed Capital Costs ($000)		Equipment Operating Costs ($/hr)
Sorber/Desorber Structure	7440		
Structural Steel		1430	--
Reinforced Concrete		5430	--
Insulation		580	--
Paper Transporter System	1840		
Basket and Rail System		1500	--
Electric Motors		340	25
Fans	915		
Sorber Forced Draft (F-101)		325	28
Sorber Induced Draft (F-102)		325	28
Air Cooler Forced Draft (F-103)		125	6
Desorber Fan (F-104)		140	6
Ljungstrom Heat Exchanger (E-101)		525	--
Duct Work (Insulated)	1740		
Sorber Inlet		325	--
Sorber Outlet		325	--
Desorber		400	--
Air Cooler		160	--
Economizer Draw-Off		400	--
Sorber By-Pass		130	--
Baffle Valves	32		
Economizer Main (B-101)		22	--
Economizer Draw-Off (B-102)		8	--
Desorber Make-Up (B-103)		1	--
SO_2 Product (B-104)		1	--
Instrumentation		80	--
Sorber Stream Quench System		15	--
Paper Storage		70	--
Paper Conveyor		90	1
Paper Shredder		50	1
	TOTAL	12,797	95

TABLE II
SULFUR DIOXIDE RECOVERY PROCESS COST BREAKDOWN
LARGE NEW POWER PLANT CASE

	($/hr)
Expenses:	
Equipment Operating Costs	95
Paper Replacement Cost	218
Depreciation (30 Year Straight-Line)	53
Maintenance (5% of Capital Investment Per Year)	81
Insurance (1% of Capital Investment Per Year)	16
Financing Interest (7% of Capital Investment Per Year)	113
Taxes (2% of Capital Investment Per Year)	32
Labor with 100% Overhead (3 Operators Per Shift)	38
Subtotal	646
Credits:	
SO_2 as Feed Stream in Sulfuric Acid Manufacture @ $10/Ton SO_2)	<357>
Spent Paper As Fuel	<142>
Subtotal	<499>
Total Operating Cost	147
(31¢/Ton Coal)	

(3) The outer surface of the sorber/desorber unit is insulated against heat losses at a cost of $2 per square foot of installed insulation material (References 11, 12, and 13).

(4) The paper transport system consists of steel mesh baskets supported on rails and powered by electric motors. The steel required in the basket support and rail system construction is costed as equivalent to the structural steel required in an office building of comparable size to the sorber. A 6800 HP electric motor with an installed cost of $340K powers the paper transport system (References 14, 15, 16, and 17).

(5) A forced draft fan (F-101) and an induced draft fan (F-102), 7500HP each, are required to overcome the 24 inches of water pressure drop in the sorber. The installed capital costs for these two fans is estimated at $325K each. The air cooler fan (F-103) and the desorber fan (F-104) are 1700HP each (References 1, 13, 18, 19, and 20).

(6) The Ljungstrom heat exchanger (E-101) is a regenerative type capable of handling 50 MMSCFH per side. The pressure drop in the Ljungstrom is approximately 3.5 - 4.0 inches WG per side with 5 percent gas leakage from the flue gas side to the desorption gas side. The heat exchanger is approximately 44 feet in diameter, 54 inches in length and weighs 225 tons. The delivered cost of the Ljungstrom is $400K and an estimated 6000 man-hours are required for installation (Reference 21).

(7) The sizing of the duct work in the sulfur dioxide recovery unit is based on a gas velocity of 2000-3000 ft/min. The ducting is constructed of 10 gauge Corten steel and has an average weight of 7-1/2 lbs per ft^2 (which includes an allowance for support steel, connections and expansion joints) and is insulated wherever heat losses are to be kept to a minimum. The duct

material is costed at 60 cents per lb for materials. The installation charge is 50 cents per lb based on 30 lbs of duct work erected per man-hour at a burdened cost of \$15/hr (References 22 and 23). The duct work included 200-foot lengths at each end of the sorber and 800 feet of duct work for the desorber section.

(8) The sulfur dioxide recovery system is depreciated on a 30-year straight line basis. The annual charges for maintenance, insurance, financing interest and taxes are costed at %5, 1%, 7% and 2% of capital investment respectively.

(9) The paper replacement rate is 36 tons per hour (0.1 wt percent per pass through the sorber) at a cost of \$6 per ton of paper (References 24 and 25). The density of waste paper is considered 70 lbs/ft^3 (Reference 26) and heat from the combustion of spent paper (7560 Btu/lb paper) is credited at 25¢/MM Btu. The conveyor carrying the paper to and from the sorber is costed as a belt type (Reference 27). The paper shredder has the capability of crushing and shredding cartons and bulky material as well as paper (Reference 28).

(10) The concentrated (9 percent) sulfur dioxide stream is credited at \$10/ton SO_2 as a feed stream to a sulfuric acid plant (\$15/ton sulfuric acid on an equivalent weight basis). The sulfur dioxide recovery process is designed to remove approximately 72,000 pounds of sulfur dioxide per hour from the power plant flue gas stream. The effect of the sulfur dioxide byproduct credit on the process operating cost is shown in Figure 12.

(11) The power plant operates at 90 percent capacity (330 days/year).

(12) Operating labor is costed at \$100,000 per operator position per year (one operator position is based on 3 shifts per day, 7 days per week, with overhead). Three operating positions should be the maximum required for the sulfur dioxide recovery system.

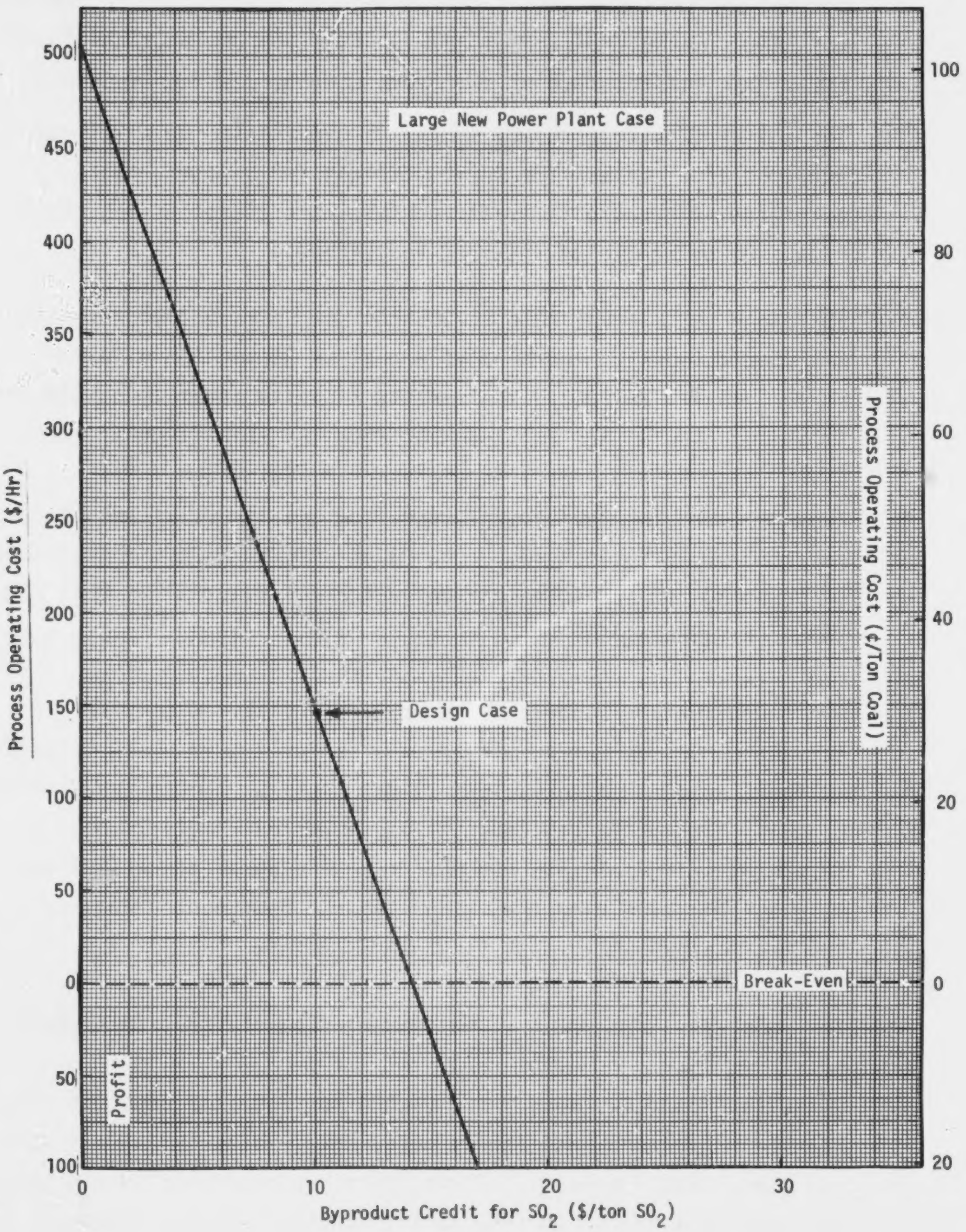


FIGURE 12. EFFECT OF SO_2 BYPRODUCT CREDIT OF THE TOTAL OPERATING COST OF THE SO_2 RECOVERY PROCESS

(13) Electrical power, at the source, is costed at 0.5¢/KWH.

5.2 LARGE EXISTING POWER PLANT CASE

The sulfur dioxide removal requirements for the large existing power plant case are the same as those for the new large power plant case and consequently, the sulfur dioxide recovery unit has essentially the same design for both cases. The sulfur dioxide recovery process for the large existing power plant case would incur all of the capital and operating costs identified for the large new power plant case and also the added costs associated with modifying the existing power plant equipment. The analysis for this case was conducted under the assumption that the power plant consists of three boiler units.

5.2.1 Process Design Analysis

The design analysis for the large existing power plant case is focused on identifying and costing modifications to the existing power plant that may be required in order to incorporate the sulfur dioxide recovery process. In a specific power plant design, the first consideration must be the availability of approximately 20 acres as close to the power plant boilers as possible on which to erect the sulfur dioxide recovery unit. For the purpose of this report, it is assumed that a site is available. Once the site has been cleared, most of the remaining modifications are centered around the power plant's boiler units.

Areas which most likely would require modification (represented by dashed lines in Figure 13) are (1) the duct work handling the flue gas between the economizer and the air preheater, (2) the air preheater, (3) the flue gas duct work exiting the air preheater, (4) the dust collector, (5) the air inlet fans, and (6) the air inlet ducting. The duct work between the economizer and the air preheater must be altered so that a draw-off and return stream amounting to about 20 percent of the total flue gas flow can be inserted. If the air prehaeter is of the recuperative type, it may be necessary to replace it with a Ljungstrom regenerative heat exchanger in order to conserve space. Since the sulfur dioxide recovery process requires that the flue gas be cooled to 215°F in the air preheater instead of the usual 300°F, it may be necessary to replace or add auxiliary heat exchange units to the existing air preheater.

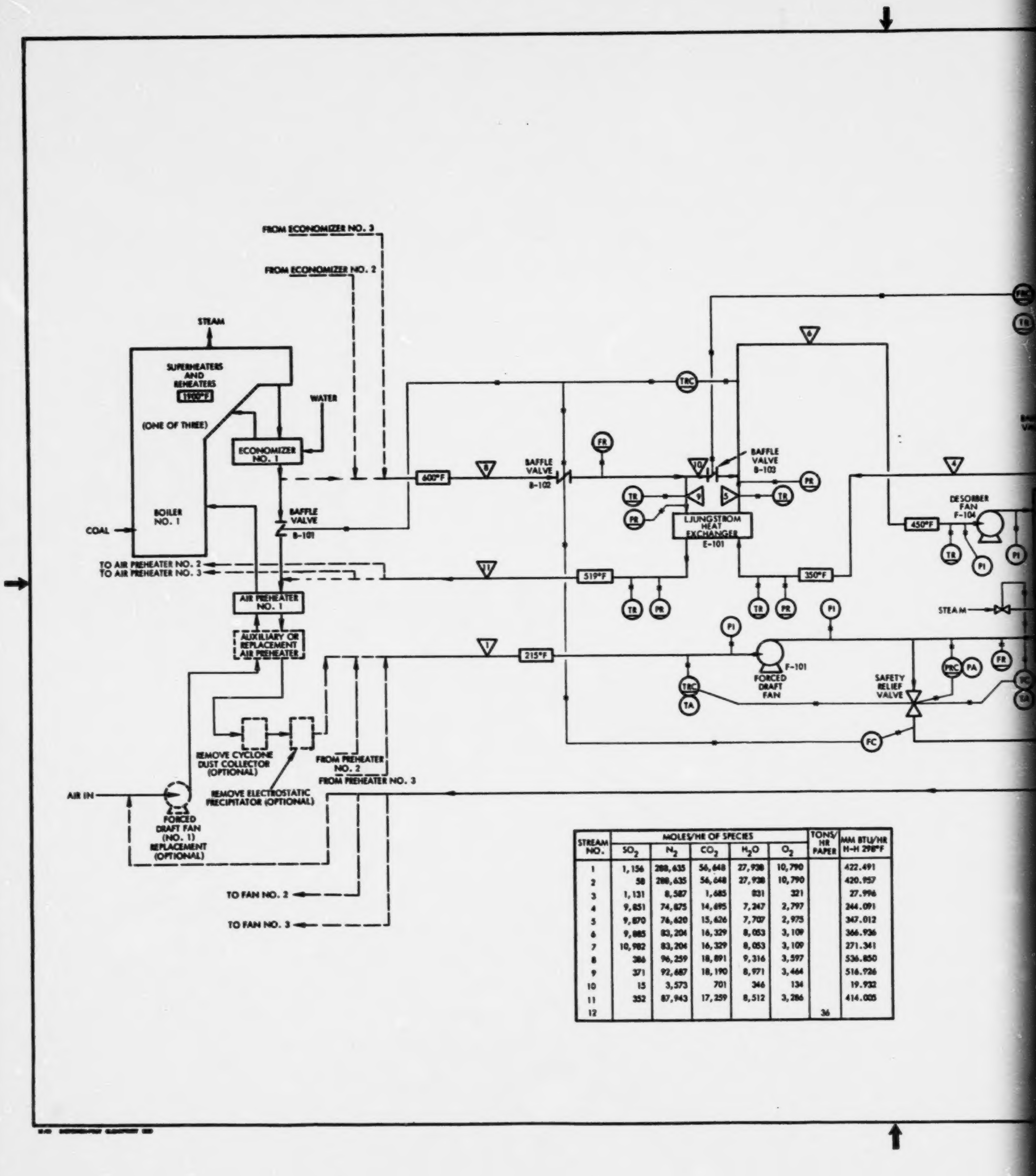
The paper in the sulfur dioxide sorber will act as a filter in removing some of the fly ash from the flue gas stream and therefore it may be economical to remove the electrostatic precipitators from the system.

The air feed supplement originating in the air cooler of the sulfur dioxide recovery system may necessitate resizing of the air inlet fans and duct work. Also the location of the stacks may not be convenient with reference to the sorber outlet and thereby add to the ducting costs.

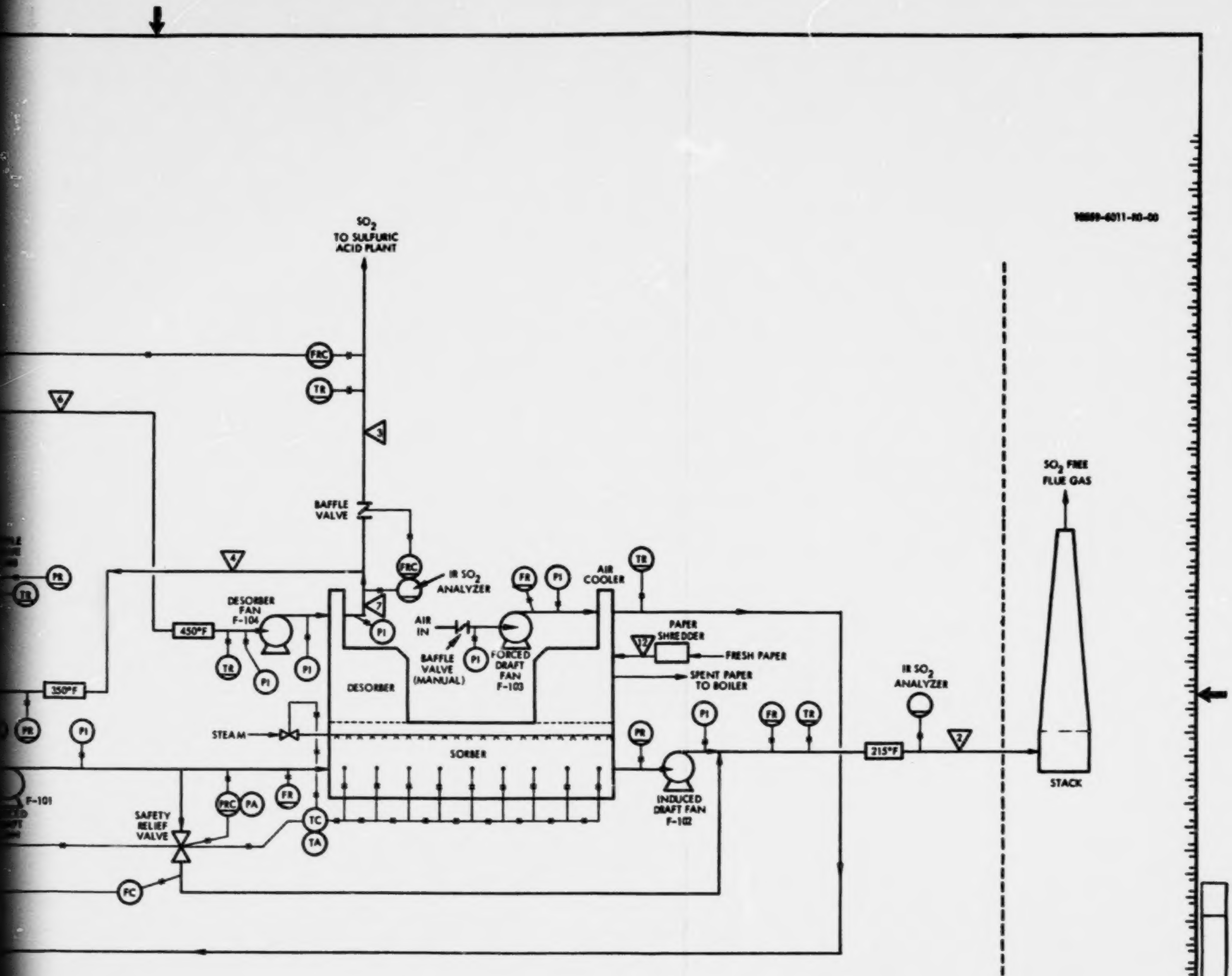
5.2.2 Economic Analysis

The installed capital and operating costs of the sulfur dioxide recovery unit alone are the same as the cost for the large new power plant case, i.e., $12.8MM in capital investment and $147/hr for operating expenses. Besides these costs, there are additional material and labor charges for adapting existing power plant equipment.

In the economic analysis, the assumption was made that the power plant consisted of three boiler units, each of which needed equipment modifications. A conservative power plant modification cost estimate (which included items such as replacing the air preheater, altering the air inlet fan capacity, removing the electrostatic precipitators and modifying the flue gas ducting around the air preheater and the economizer) was placed at $2.7 MM for material and $2.07 MM for labor charges (Table III). If only the cost of modifying the ducting in the power plant to fit the requirements of the sulfur dioxide recovery unit is considered, a material cost of $0.35 MM with an additional $0.54 MM for labor is estimated. In costing the modifications to the existing power plant, the material items were listed at regular purchased costs while the labor estimates were increased over the nominal rates to account for old equipment removal and new equipment alignment problems.


FROM ECONOMIZER NO. 3
FROM ECONOMIZER NO. 2
STEAM
SUPERHEATERS AND REHEATERS
1900°F
WATER
(ONE OF THREE)
ECONOMIZER NO. 1
BOILER NO. 1
COAL
BAFFLE VALVE
B-101
600°F
8
BAFFLE VALVE
B-102
FR
TRC
6
10
BAFFLE VALVE
B-103
TR
PR
9
5
LJUNGSTROM HEAT EXCHANGER
E-101
4
DESORBER FAN
F-104
450°F
PI
FRC
TO AIR PREHEATER NO. 2
TO AIR PREHEATER NO. 3
11
519°F
350°F
AIR PREHEATER NO. 1
AUXILIARY OR REPLACEMENT AIR PREHEATER
7
215°F
F-101
FORCED DRAFT FAN
TRC
TA
SAFETY RELIEF VALVE
STEAM
PRC
PA
FC
REMOVE CYCLONE DUST COLLECTOR (OPTIONAL)
REMOVE ELECTROSTATIC PRECIPITATOR (OPTIONAL)
FROM PREHEATER NO. 2
FROM PREHEATER NO. 3
AIR IN
FORCED DRAFT FAN (NO. 1) REPLACEMENT (OPTIONAL)
TO FAN NO. 2
TO FAN NO. 3

STREAM NO.	MOLES/HR OF SPECIES					TONS/HR PAPER	MM BTU/HR H-H 298°F
	SO_2	N_2	CO_2	H_2O	O_2		
1	1,156	288,635	56,648	27,938	10,790		422.491
2	58	288,635	56,648	27,938	10,790		420.957
3	1,131	8,587	1,685	831	321		27.996
4	9,851	74,875	14,695	7,247	2,797		244.091
5	9,870	76,620	15,626	7,707	2,975		347.012
6	9,885	83,204	16,329	8,053	3,109		366.936
7	10,982	83,204	16,329	8,053	3,109		271.341
8	386	96,259	18,891	9,316	3,597		536.850
9	371	92,687	18,190	8,971	3,464		516.926
10	15	3,573	701	346	134		19.932
11	352	87,943	17,259	8,512	3,286		414.005
12						36	


SO$_2$ TO SULFURIC ACID PLANT
FRC
TR
3
6
BAFFLE VALVE
4
PR
TR
FRC
IR SO$_2$ ANALYZER
7
DESORBER FAN F-104
450°F
TR
PI
PI
PI
350°F
PR
PI
AIR IN
BAFFLE VALVE (MANUAL)
PI
FORCED DRAFT FAN F-103
FR
PI
AIR COOLER
TR
PAPER SHREDDER
12
FRESH PAPER
SPENT PAPER TO BOILER
DESORBER
STEAM
SORBER
PR
INDUCED DRAFT FAN F-102
PI
FR
TR
215°F
IR SO$_2$ ANALYZER
2
SO$_2$ FREE FLUE GAS
STACK
F-101
SAFETY RELIEF VALVE
PRC
PA
FR
TC
TA
FC

O_2	TONS/ HR PAPER	MM BTU/HR H-H 298°F
0,790		422.491
0,790		420.957
321		27.996
2,797		244.091
2,975		347.012
3,109		366.936
3,109		271.341
3,597		536.850
3,464		516.926
134		19.932
3,256		414.005
	36	

KEY FOR INSTRUMENTATION

○	MOUNTED LOCALLY
⊖	MOUNTED IN CONTROL ROOM
FR	FLOW RECORDER
FRC	FLOW RECORDER CONTROLLER
PA	PRESSURE ALARM
PI	PRESSURE INDICATOR
PR	PRESSURE RECORDER
PRC	PRESSURE RECORDER CONTROLLER
TA	TEMPERATURE ALARM
TC	TEMPERATURE CONTROLLER
TI	TEMPERATURE INDICATOR
TR	TEMPERATURE RECORDER
TRC	TEMPERATURE RECORDER CONTROLLER

TRW

Figure 13

LARGE EXISTING
POWER PLANT FLOW DIAGRAM

D 11982

TABLE III

EQUIPMENT MODIFICATION, CAPITAL AND OPERATING COST BREAKDOWN

LARGE EXISTING POWER PLANT CASE

	EQUIPMENT MODIFICATION CHARGES ($000)		INSTALLED CAPITAL CHARGES ($000)	OPERATING COST ($/HR)
Sulfur Dioxide Sorber/Desorber System			12,797	95
Possible Modifications to Large Existing Power Plant (Three Boilers)	Material	Labor		
Replace Air Preheater	2190	1470	3,660	
Modify Air Inlet Fans	150	30	180	
Remove Electrostatic Precipitators	-	30	30	
Modify Ducting				
Post Economizer Draw-Off	165	225	390	
Pre Air Preheater Return	165	225	390	
Air Inlet	24	90	114	
Conservative Total	2694	2070	17,561	95
Optimistic Total (Modification to Ducting Only)	354	540	13,691	95

When the power plant modification costs are combined with the capital and operating costs associated with the sulfur dioxide recovery system, a conservative total capital cost of $17.6 MM and an optimistic capital cost of $13.7 MM are estimated for incorporating the recovery system into a large existing power plant. The equipment operating cost remains at $95 per hour.

The sulfur dioxide recovery cost breakdown for the large existing power plant case (Table IV) resulted in a total operating cost of $168 per hour (35¢/ton coal) as an optimistic cost and $257 per hour (54¢/ton coal) when costed conservatively. The effect of the sulfur dioxide by-product credit on the overall process operating cost is shown in Figure 14.

5.3 SMALL EXISTING POWER PLANT CASE

The sulfur dioxide recovery process for the small existing power plant case is designed to remove and recover 90 percent of the sulfur dioxide present in a flue gas stream flowing at 0.5 MM SCFM. This flue gas rate would correspond to a power plant generating approximately 225 Megawatts of electrical power and consuming 100 tons of coal per hour as fuel. A 225 Megawatt power plant is estimated to require a site of 100 acres. The sulfur dioxide recovery unit will occupy approximately 3.5 acres as near to the boiler units as possible.

5.3.1 Process Design Analysis

The process design of the sulfur dioxide recovery system followed the same analysis path as described for the large new power plant case. First a process flowsheet and a mass and energy balance were determined for the sorption system (Figure 15). Then the sorption mathematical model was used to determine the volume of the sorber.

In this case, the mass fraction of sulfur dioxide in the flue gas entering the sorber is 6.58×10^{-3} lbs SO_2 lb flue gas and 90 percent of this is removed by sorption on paper. The sulfur on the paper entering the sorber is assumed negligible. Using this information and the flue

TABLE IV
SULFUR DIOXIDE RECOVERY PROCESS COST BREAKDOWN
LARGE EXISTING POWER PLANT CASE

	OPTIMISTIC ($/HR)	CONSERVATIVE ($/HR)
Expenses:		
Equipment Operating Costs	95	95
Paper Replacement Cost	218	218
Depreciation (30-Year Straight-Line)	57	73
Maintenance (5% of Capital Investment Per Year)	86	111
Insurance (1% of Capital Investment Per Year)	17	22
Financing Interest (7% of Capital Investment Per Year)	121	155
Taxes (2% of Capital Investment Per Year	35	44
Labor With 100% Overhead (3 Operators Per Shift)	38	38
Subtotal	667	756
Credits:		
SO_2 as Feed Stream in Sulfuric Acid Manufacture (@ $10/Ton SO_2)	(357)	357
Spent Paper as Fuel	(142)	142
Subtotal	(499)	499
Total Operating Cost	168	257
	(35¢/Ton Coal)	(54¢/Ton Coal)

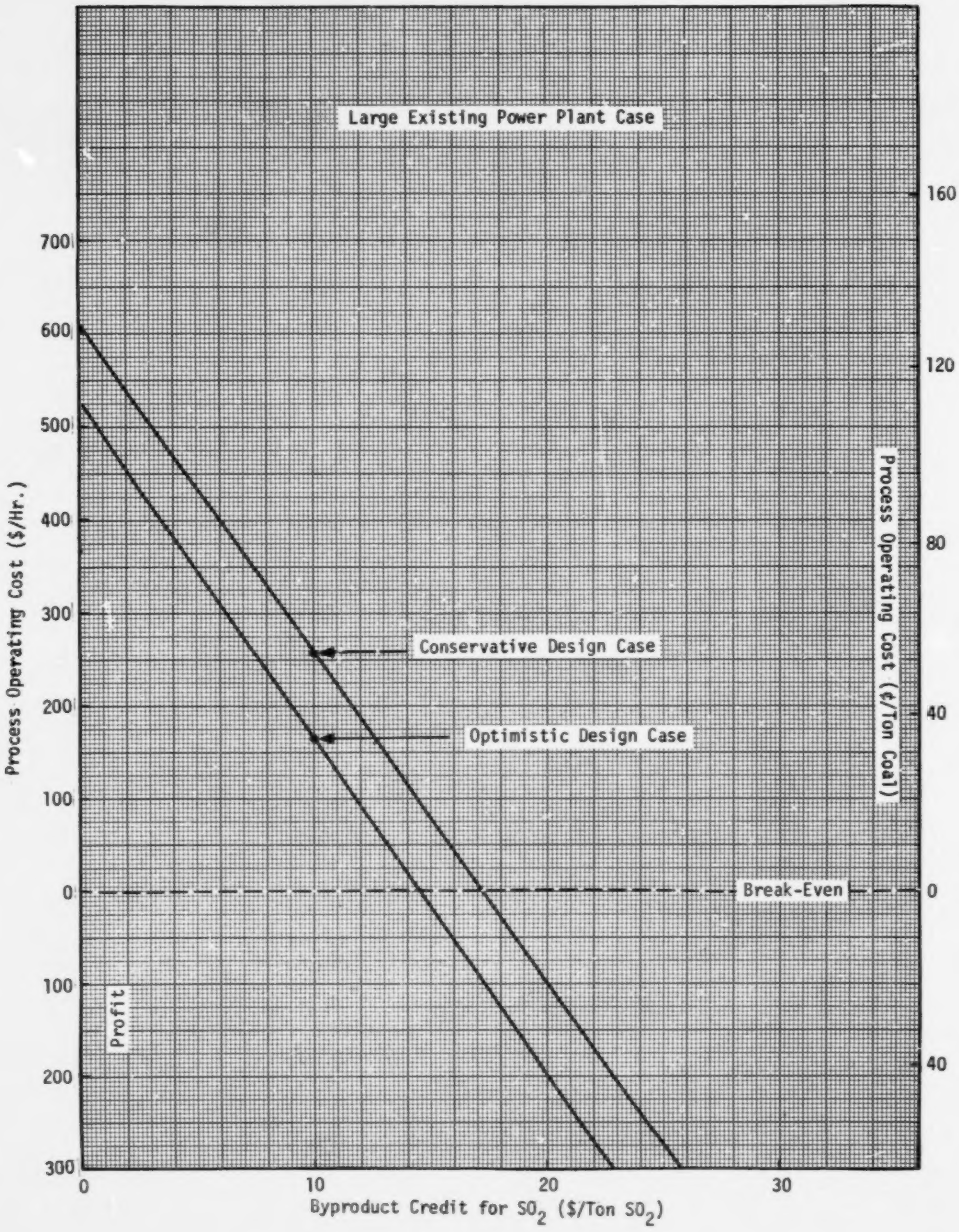
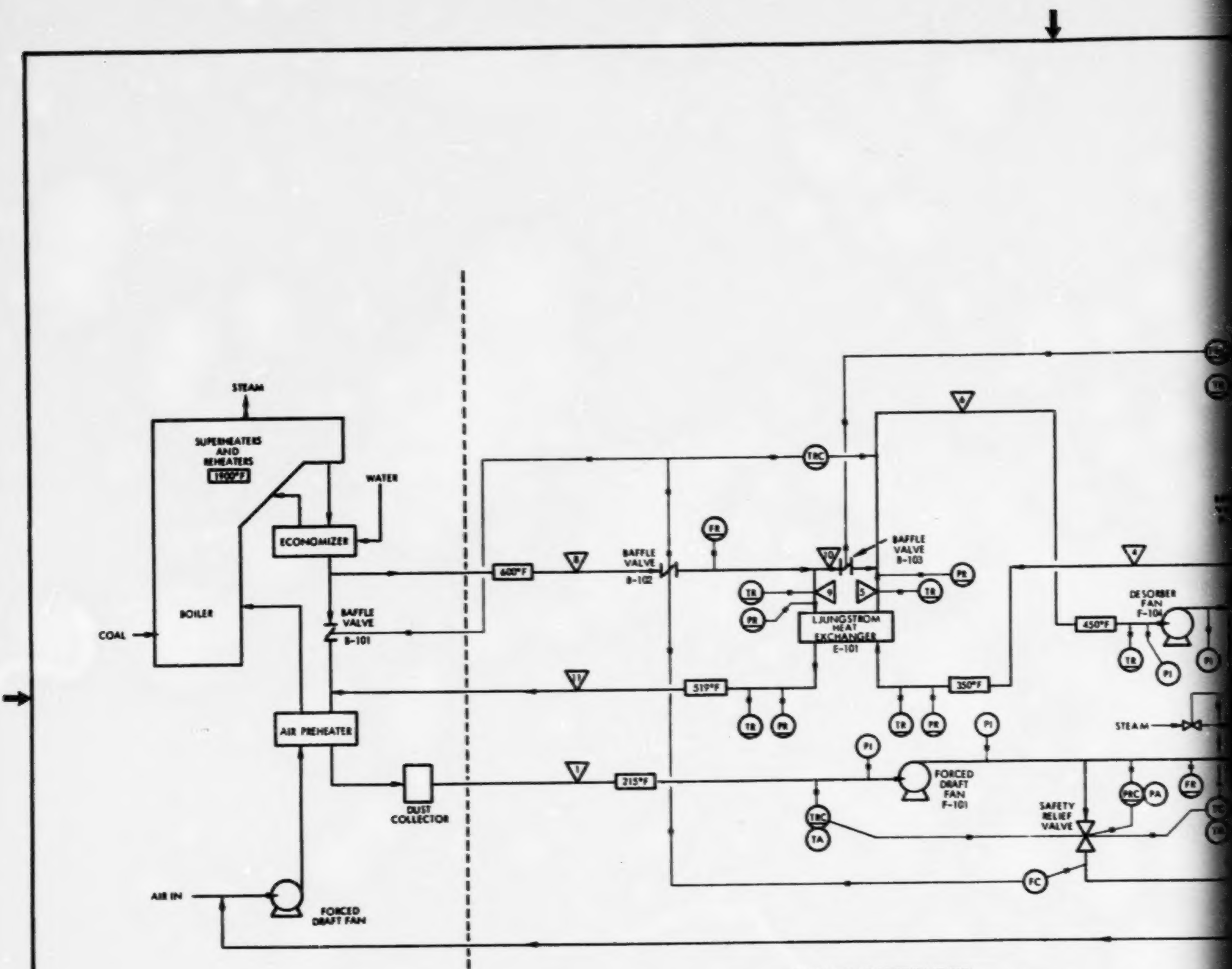
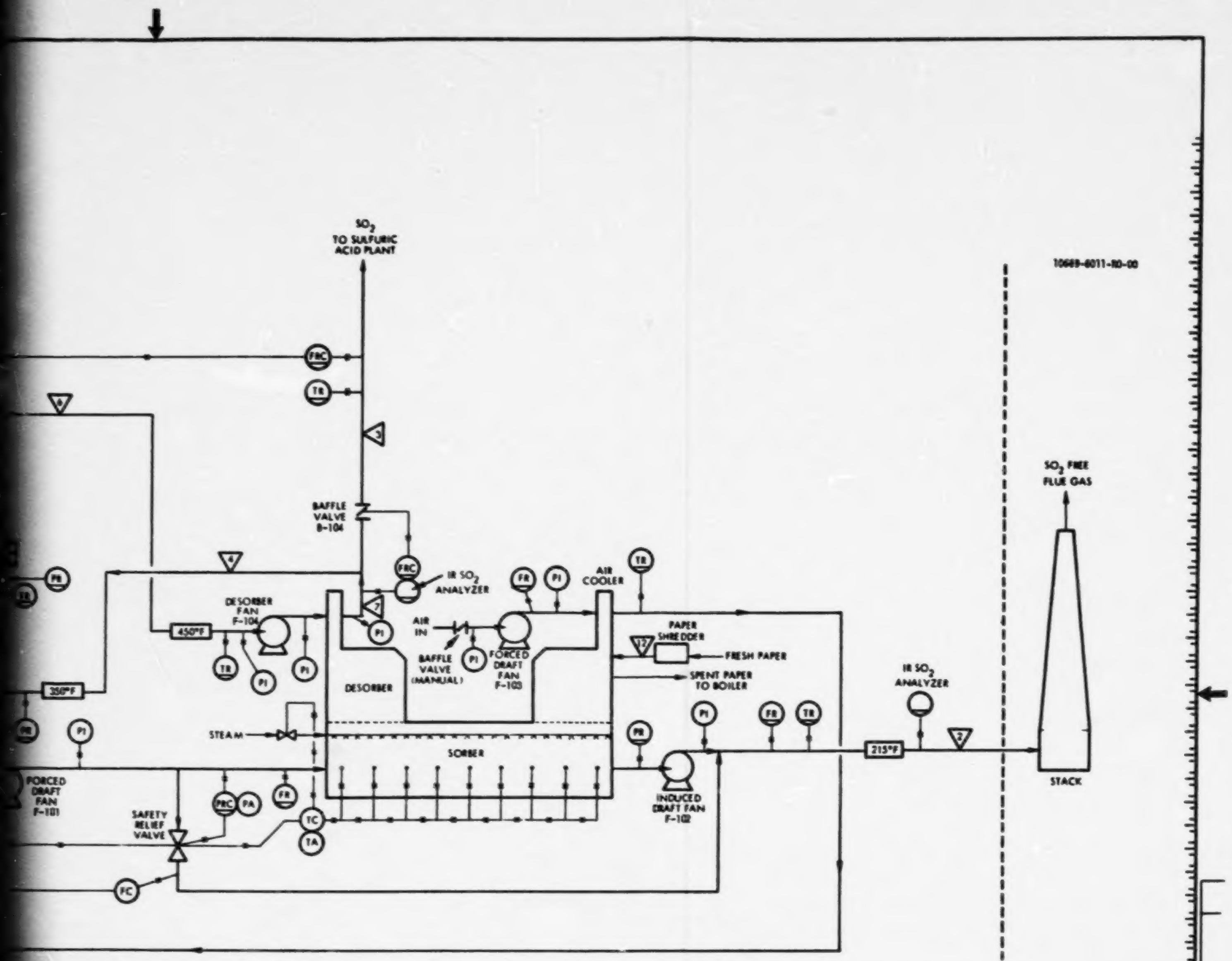


FIGURE 14. Effect of SO_2 Pyrpoduct Credit on the Total Operating Cost of the SO_2 Recovery Process


STEAM
SUPERHEATERS AND REHEATERS
1900°F
WATER
ECONOMIZER
BOILER
COAL
BAFFLE VALVE B-101
AIR PREHEATER
DUST COLLECTOR
AIR IN
FORCED DRAFT FAN
600°F
8
BAFFLE VALVE B-102
FR
TRC
10
BAFFLE VALVE B-103
TR
PR
9
5
LJUNGSTROM HEAT EXCHANGER E-101
6
4
DESORBER FAN F-104
450°F
PI
11
519°F
350°F
7
215°F
FORCED DRAFT FAN F-101
TA
SAFETY RELIEF VALVE
PRC
PA
FC

SMALL EXISTING POWER PLANT CASE

STREAM NO.	MOLES/HR OF SPECIES SO_2	N_2	CO_2	H_2O	O_2	TONS/HR PAPER	MM BTU/HR H - H 298°K
1	232	57,776	11,339	5,592	2,159		84.568
2	23	57,776	11,339	5,592	2,159		84.277
3	214	1,666	327	161	62		5.416
4	1,972	14,985	2,941	1,451	559		48.852
5	1,975	15,938	3,127	1,542	595		69.451
6	1,978	16,652	3,268	1,612	622		73.435
7	2,186	16,652	3,268	1,612	622		54.272
8	76	19,268	3,780	1,864	719		107.440
9	73	18,553	3,640	1,795	693		103.456
10	3	715	139	69	26		3.979
11	69	17,603	3,454	1,703	658		82.857
12						6.8	


SO$_2$ TO SULFURIC ACID PLANT
10689-6011-R0-00
FRC
TR
3
6
4
BAFFLE VALVE B-104
FRC
IR SO$_2$ ANALYZER
PR
TR
DESORBER FAN F-104
450°F
TR
PI
PI
7
PI
AIR IN
BAFFLE VALVE (MANUAL)
PI
FORCED DRAFT FAN F-103
FR
PI
AIR COOLER
TR
PAPER SHREDDER
12
FRESH PAPER
SPENT PAPER TO BOILER
DESORBER
350°F
PR
PI
STEAM
SORBER
FORCED DRAFT FAN F-101
SAFETY RELIEF VALVE
PRC
PA
FR
TC
TA
FC
PR
INDUCED DRAFT FAN F-102
PI
FR
TR
IR SO$_2$ ANALYZER
215°F
2
SO$_2$ FREE FLUE GAS
STACK

CASE

TONS/HR PAPER	MM BTU/HR H - H 298°K
	84.568
	84.277
	5.416
	48.852
	69.451
	73.435
	54.272
	107.440
	103.456
	3.979
	82.857
6.8	

KEY FOR INSTRUMENTATION

○ MOUNTED LOCALLY

⊖ MOUNTED IN CONTROL ROOM

FR	FLOW RECORDER
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TC	TEMPERATURE CONTROLLER
TI	TEMPERATURE INDICATOR
TR	TEMPERATURE RECORDER
TRC	TEMPERATURE RECORDER CONTROLLER

TRW
ONE SPACE PARK · REDONDO BEACH, CALIFORNIA

Figure 15

SMALL EXISTING
POWER PLANT FLOW DIAGRAM

SIZE D
CODE IDENT NO. 11982
SCALE
SHEET

gas flow rate into the sorber, the mathematical model was used to generate the sorber volume as a function of the sulfur dioxide on the paper exiting the sorber (Figure 16). The design case, which specifies a sorber volume of approximately 650,000 ft^3, was selected after an iterative design analysis involving other parameters, such as pressure drop, paper velocity, etc.

The Ergun equation (Equation 10) was used in the pressure drop evaluation. The pressure drop through the sorber was specified at 24 inches of H_2O and a relationship was determined between the paper particle size (actually the particle diameter of an equivalent sphere) and the allowable sorber length, with the void fraction in the sorber as a parameter (Figure 17). The indicated design case, based on an equivalent particle diameter of 0.5 inches and a void fraction of 0.9, has an allowable sorber length of 350 ft (and therefore a square cross-section of 45 feet on a side).

Other parameters of interest which apply to the design of the sulfur dioxide recovery process for the small existing power plant case are:

- Amount of sulfur dioxide recovered is approximately 13,000 lbs/hr.
- Total weight of the paper packing in the sorber is 2,250 tons
- Velocity of the flue gas in the sorber is 356 ft/min
- Velocity of the paper bed is 16 ft/min

The mass fraction of sulfur dioxide in the flue gas and on the paper as a function of distance along the sorber (Figure 18) was calculated using the sorption mathematical model.

Desorption is carried out at 450°F and the desorption gas stream is maintained at 9 percent sulfur dioxide. In the design case, the paper replacement rate is 0.1 percent by weight during each cycle through the sorber or 6.8 tons paper per hour.

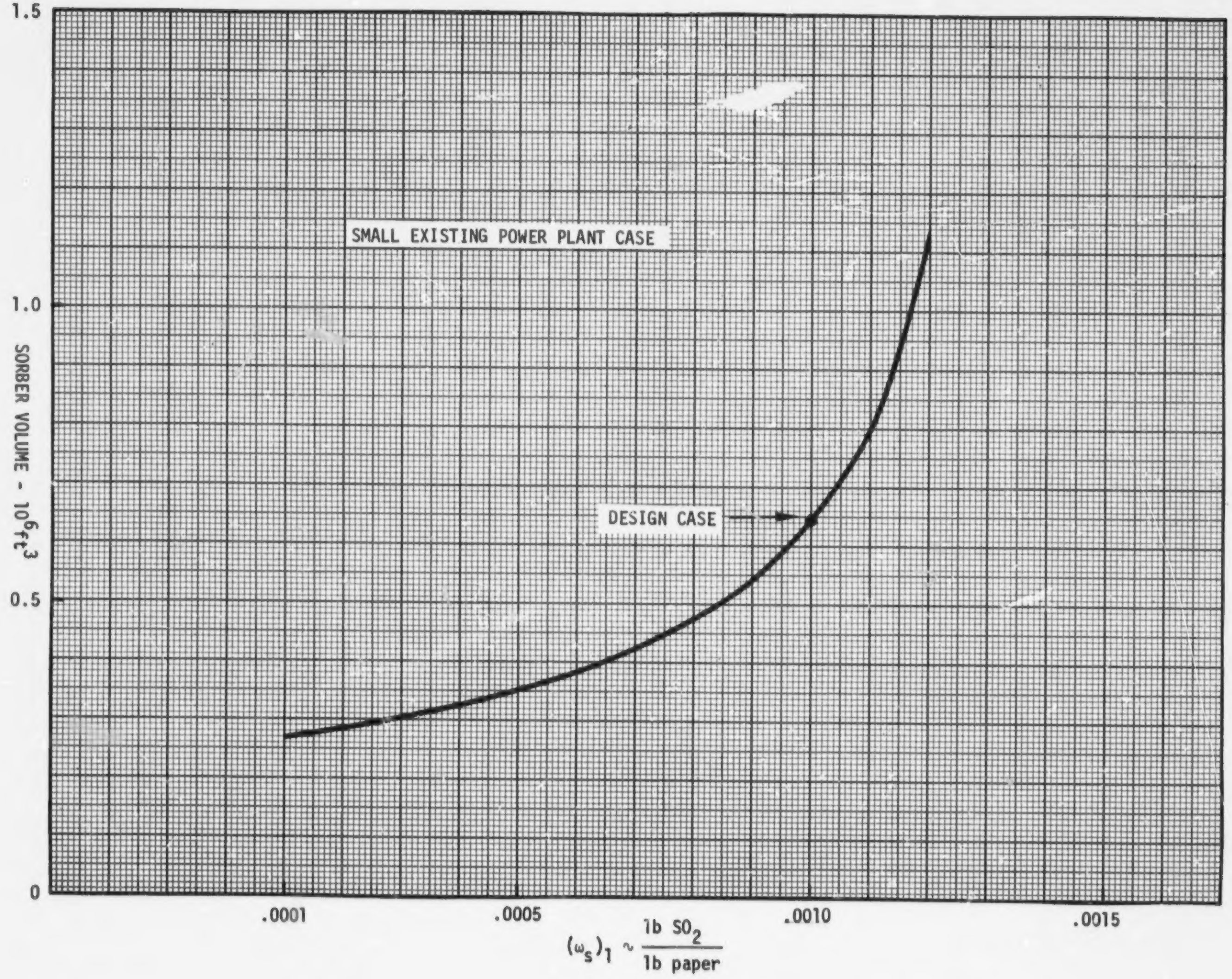
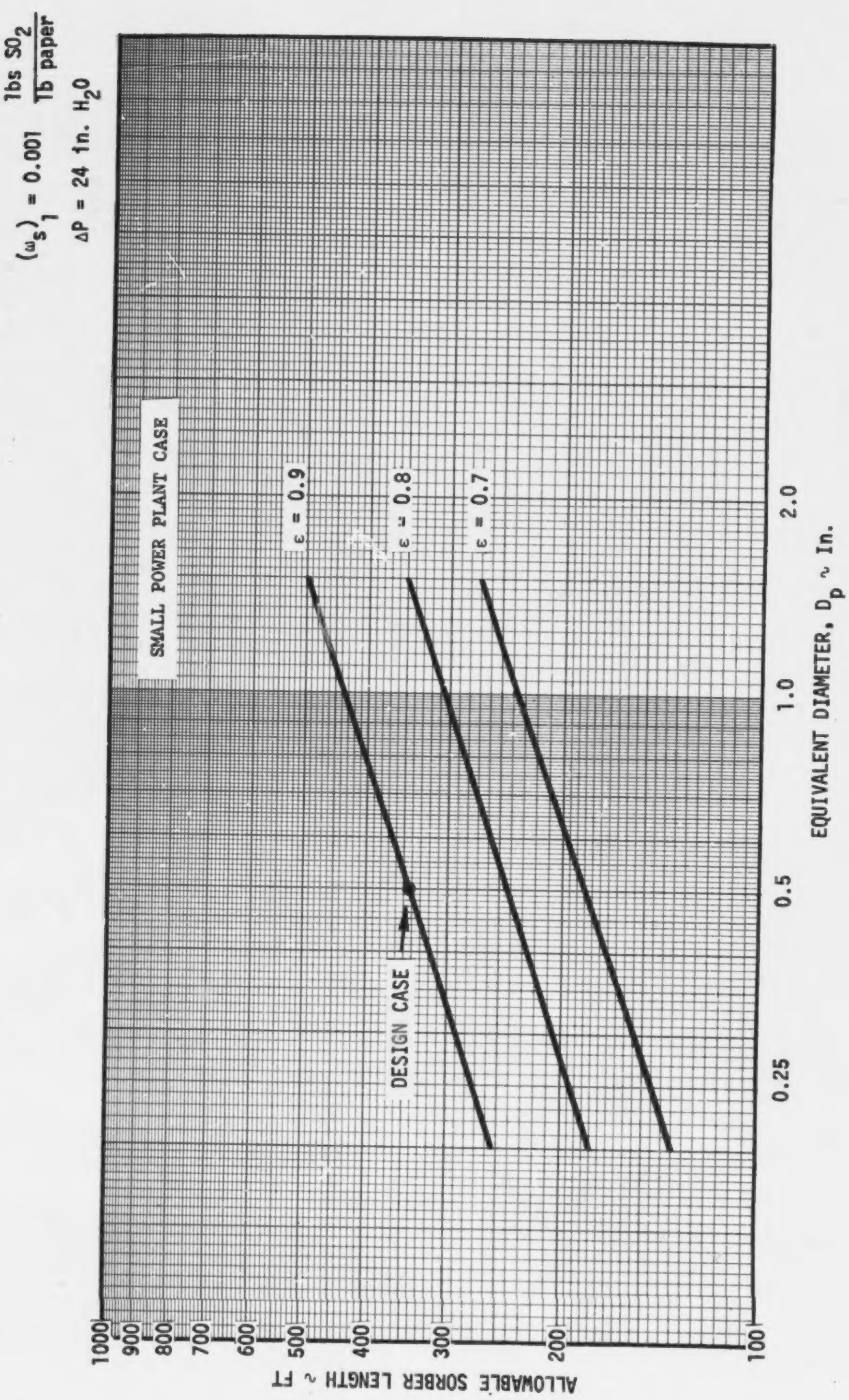


Figure 16. Mass Fraction of SO_2 on Paper Exiting from Sorber vs. Volume of Sorber


$(\omega_s)_1 = 0.001 \ \frac{\text{lbs SO}_2}{\text{lb paper}}$

$\Delta P = 24$ in. H_2O

Figure 17. Equivalent Diameter of Paper Packing vs. Sorber Length

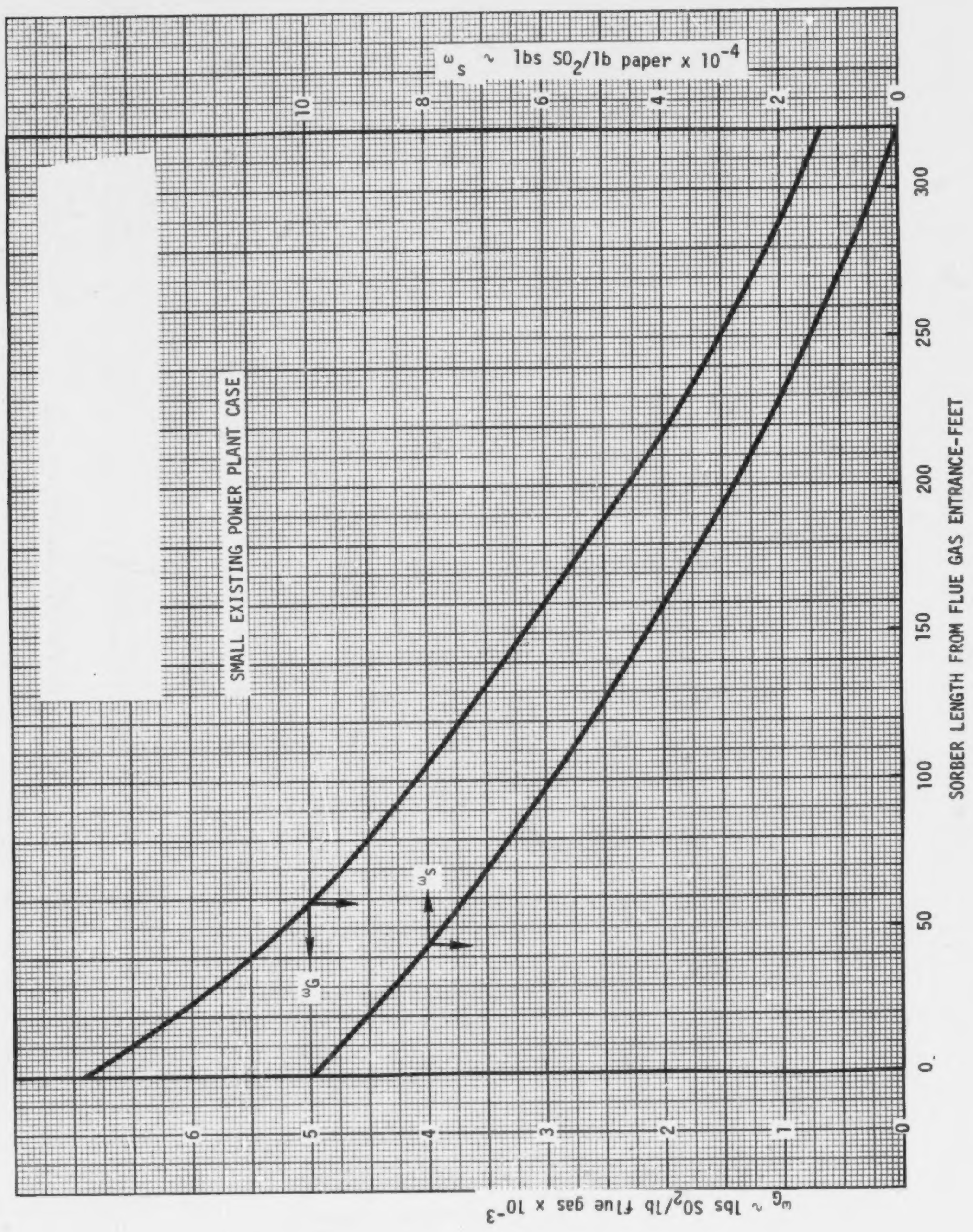


Figure 18. Mass Fraction of SO_2 on Paper Exiting from Sorber vs. Volume of Sorber

Since the design analysis pertains to an existing plant, modifications to the boiler units were also considered. The same areas identified in the large existing power plant case (i.e., flue gas ducting in the boiler unit, air preheater, dust collector, air inlet fans) may require modification. For design and costing purposes, the power plant is assumed to consist of two boiler units.

5.3.2 Economic Analysis

The economic analysis for the small existing power plant case was directed towards estimating the capital and operating costs associated with the sulfur dioxide recovery process equipment and also the material and labor charges incurred in incorporating the recovery unit into the existing power plant. The results of the study show that the installed capital and equipment operating costs for only the sulfur dioxide recovery unit are \$3.4 MM and \$22/hr respectively (Table V). If only the sulfur dioxide recovery unit is considered, the total process operating cost including paper replacement, depreciation, labor, sulfur dioxide credit, etc., is \$71/hr or 71¢/ton coal (Table VI).

Estimates of the costs associated with adapting the exiting power plant so that it accomodates the sulfur dioxide recovery unit were based on a power plant having two boiler units, each of which requires modification. A conservative modification cost (which includes items such as replacing the boiler unit's air preheater, altering the air inlet fan capacity, removing electrostatic precipitators and modifying the flue gas ducting between the air preheater and economizer) was estimated at \$326K for materials and \$427K for labor. An optimistic estimate which is based on the charges for modifying the duct work only is costed at \$90K for materials with an additional \$142K for labor (Table VII). Combining the power plant modification costs with the capital costs of the sulfur dioxide recovery system results in a conservative capital investment of \$4.18 MM and an optimistic investment of \$3.66 MM.

TABLE V

EQUIPMENT CAPITAL AND OPERATING COST BREAKDOWN
SMALL EXISTING POWER PLANT CASE
SULFUR DIOXIDE RECOVERY SYSTEM ONLY

	Installed Capital Costs ($000)		Operating Costs ($/hr)
Sorber/Desorber Structure	1585		
Structural Steel		240	--
Reinforced Concrete		1170	--
Insulation		175	--
Paper Transporter System	310		
Basket and Rail System		240	
Electric Motors		70	4
Fans	350		
Sorber Forced Draft (F-101)		125	6.50
Sorber Induced Draft (F-102)		125	6.50
Air Cooler Forced Draft (F-103)		50	2
Desorber Fan (F-104)		50	2.50
Ljungstrom Heat Exchanger (E-101)		80	--
Duct Work (Insulated)	830		
Sorber Inlet		150	--
Sorber Outlet		150	--
Desorber		190	--
Air Cooler		190	--
Economizer Draw-Off		60	--
Sorber By-Pass		90	--
Baffle Values	9		
Economizer Main (B-101)		5.5	--
Economizer Draw-Off (B-102)		2.0	--
Desorber Make-up (B-103)		0.75	--
SO_2 Product (B-104)		0.75	--
Instrumentation		70	--
Sorber Steam Quench System		15	--
Paper Storage		70	
Paper Conveyor		90	0.25
Paper Shredder		15	0.25
	TOTAL	3424	22.00

TABLE VI
SULFUR DIOXIDE RECOVERY PROCESS COST BREAKDOWN
SMALL EXISTING POWER PLANT CASE
(Without Modification to Existing Power Plant)

		($/hr)
Expenses:		
Equipment Operating Costs		22
Paper Replacement Cost		41
Depreciation (30 Year Straight-Line)		14
Maintenance (5% of Capital Investment Per Year)		22
Insurance (1% of Capital Investment Per Year)		4
Financing Interest (7% of Capital Investment Per Year)		30
Taxes (2% of Capital Investment Per Year)		8
Labor With 100% Overhead (2 Operators Per Shift)		25
	Subtotal	166
Credits:		
SO_2 As Feed Stream in Sulfuric Acid Manufacture (@ $10/Ton SO_2)		<69>
Spent Paper as Fuel		<26>
	Subtotal	<95>
	Total Operating Cost (71¢/Ton Coal)	71

TABLE VII

EQUIPMENT MODIFICATION, CAPITAL AND OPERATING COST BREAKDOWN

SMALL EXISTING POWER PLANT CASE

	EQUIPMENT MODIFICATION CHARGES ($000)		INSTALLED CAPITAL CHARGES ($000)	OPERATING COST ($/HR)
	Material	Labor		
Sulfur Dioxide Sorber/Desorber System			3,424	22
Possible Modifications to Small Existing Power Plant (Two Boilers)				
Replace Air Preheater	210	260	470	
Modify Air Inlet Fans	26	5	31	
Remove Electrostatic Precipitators	--	20	20	
Modify Ducting				
Post Economizer Draw-Off	42	62	104	
Pre-Air Preheater Return	42	62	104	
Air Inlet	6	18	24	
Conservative Total	326	427	4,177	22
Optimistic Total (Modification to Ducting Only)	90	142	3,656	22

The total cost breakdown for the sulfur dioxide recovery system installed in an existing small power plant (Table VIII) estimates the total process operating cost between \$77 per hour (77¢/ton coal) and \$89 per hour (89¢/ton coal combusted).

The cost considerations used in the economic analysis of the small existing power plant are presented below:

(1) The superstructure of the sorber, constructed of reinforced concrete, is 2025 square feet in cross section and 350 feet in length. An additional volume of 360,000 cubic feet is required for the air cooling and desorption sections. The foundation concrete, poured to a thickness of 8 feet, is costed at \$55 per cubic yard; the wall concrete, an average of 1.5 feet thick, is costed at \$115 per cubic yard; and the prestressed concrete roof, 2 feet thick, costs \$185 per cubic yard (Reference 9). Twelve concrete buttresses used for support cost a total of \$40K.

(2) The structural steel used in construction of the sorber and the "paper" basket network is costed as being equivalent to a 4 story office building (i.e., 11 lbs steel for equivalent square foot). The structural steel is priced at \$350/ton installed (Reference 10). The outer surfaces are insulated against heat losses at a cost of \$2 per square foot (References 11, 12, and 13).

(3) The paper transporter system requires 500 tons of structural steel in the basket and rail construction. (The amount of steel is comparable to that required in an office building if the same size as the sorber system.) A 1000 HP electric motor having an installed cost of \$70K powers the paper transport system (References 14, 15, 16, and 17).

TABLE VIII
SULFUR DIOXIDE RECOVERY COST BREAKDOWN
SMALL EXISTING POWER PLANT CASE
(With Modification to Existing Power Plant)

	Optimistic ($/Hr.)	Conservative ($/Hr.)
Expenses:		
Equipment Operating Costs	22	22
Paper Replacement Cost	41	41
Depreciation (30 Year Straight-Line)	15	17
Maintenance (5% of Capital Investment Per Year)	23	26
Insurance (1% of Capital Investment Per Year)	5	5
Financing Interest (7% of Capital Investment Per Year)	32	37
Taxes (2% of Capital Investment Per Year)	9	11
Labor with 100% Overhead (2 Operators Per Shift)	25	25
Subtotal	172	184
Credits:		
SO_2 as Feed Stream in Sulfuric Acid Manufacture (@ $10/Ton SO_2)	69	69
Spent Paper as Fuel	26	26
Subtotal	95	95
Total Operating Costs	77	89
	(77¢/Ton Coal)	(89¢/Ton Coal)

(4) The sorber fans, (F-101) and (F-103) are 1750 HP each and cost \$250K (References 1, 13, 18, 19, and 20). The desorber and air cooler fans, (F-104) and (F-103) respectively, are 530 HP each.

(5) The Ljungstrom regenerative heat exchanger (E-101) costs \$47K delivered and requires 1800 man hours to install (Reference 21). The pressure drop through the Ljungstrom is approximately 3 inches WG and the gas leakage is approximately 5 percent from the flue gas side to the desorption gas side. The heat exchanger has an outside diameter of 19 feet; the heating element height is 22 inches; and the weight is 60 tons.

(6) The sizing of the duct work for the sulfur dioxide recovery process is based on a gas velocity of 2000 ft/min. The ducting has an average weight of 7-1/2 lbs per ft^2 and costs 60 cents per lb for material and 50 cents per lb for labor charges (References 22 and 23). The lengths of ducting include 400 feet leading to and from the sorber and 600 feet in the air cooler and desorber sections.

(7) The sulfur dioxide recovery system is depreciated on a 30-year straight-line basis. The annual charges for maintenance, insurance, financing interest and taxes are costed at %5, 1%, and 2% of capital investment respectively.

(8) Fresh paper is added at a rate of 6.8 tons/hr at a cost of \$6 per ton. Spent paper is credited as fuel at 25¢/MM Btu.

(9) The sulfur dioxide recovered is credited at \$10/ton (corresponds to \$15/ton sulfuric acid). The effect of the sulfur dioxide byproduct credit on the process operating cost is shown in Figure 19.

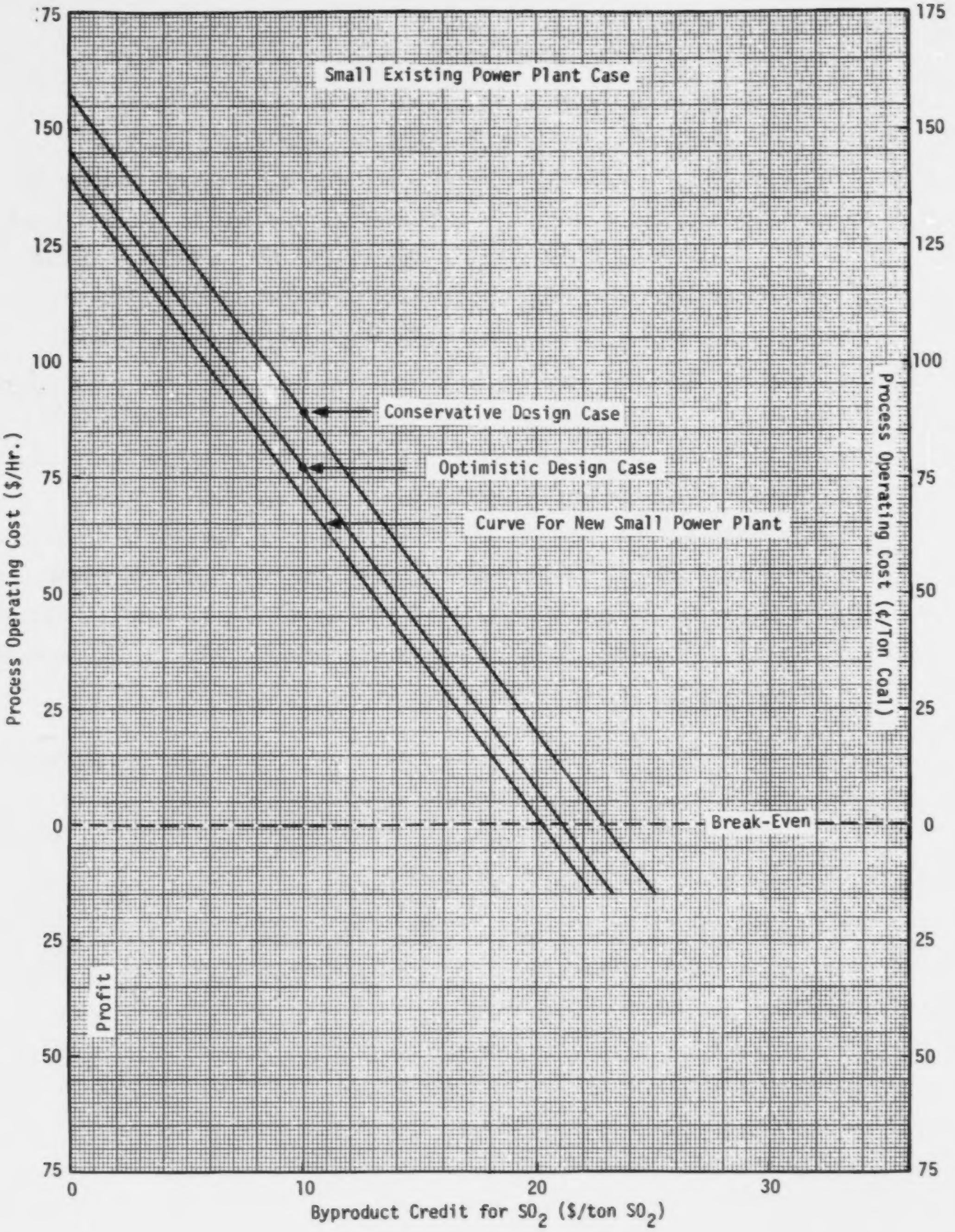


Figure 19. Effect of SO_2 Byproduct Credit on the Operating Cost of the SO_2 Recovery Process

(10) The power plant operates at 90 percent capacity (330 days per year).

(11) Two operating positions are required at a cost of $100,000 per year per position.

(12) Electrical power at the source is costed at 0.5¢/KWH.

In costing the modifications to the existing power plant, capital items were priced at regular rates but labor costs were increased over nominal charges to account for old equipment removal and new equipment alignment problems.

5.4 NEW SMELTER CASE

It is estimated that primary copper, zinc and lead smelters in the United States emit approximately 2 million tons of sulfur into the atmosphere each year. Copper smelters are the major contributors to the sulfur dioxide pollution problem and therefore the new smelter case has been directed toward the control of sulfur dioxide emissions from a copper smelter source.

5.4.1 Copper Smelter Model

A design model which is representative of the copper smelting industry (References 29 and 30) was developed to identify flue gas streams requiring sulfur dioxide pollution control. The selected copper smelter design model employs three pyrometallurgical operations: 1) roasting of the copper-containing ore in air to decrease the sulfur content; 2) smelting of copper ores in a reverberating furnace to convert the copper into a sulfide form through chemical reaction with pyrite and ferrous sulfide, and 3) oxidizing of cuprous sulfide in the converter coupled with the reaction of cuprous sulfide and cuprous oxide to form blister copper (98-99.5% Cu). The operation of the copper smelter design model is decribed below.

In the roaster, the ore which consists mainly of copper, iron and sulfur is heated in the presence of air to just below the fusion temperature (approximately 1200°F) causing the sulfur to be oxidized to sulfur dioxide and partially eliminated from the ore charge. The object of roasting is to control the amount of sulfur in the ore so that the charge when smelted will yield a matte which is richer in copper thereby reducing operating costs in the reverberating furnace and converter. Roasting is employed when the feed material is low in copper and high in iron and sulfur; nearly half the copper smelters in the U.S. roast the ore charge before it is fed to the reverberatory furnace for smelting. The roaster flue gas stream is cooled to approximately 600°F by water sprays and air dilution. The flue dust is removed by passing the gas through large chambers to lower the velocity and allow the coarsest flue dust to settle out followed by the use of Cottrell electrostatic precipitators to remove the fines.

Roasters can be the source of relatively high concentration sulfur dioxide gas streams which in some cases are used directly as a feed stream in the manufacture of sulfuric acid. But in the new smelter design case the roaster flue gas is considered as a portion of the feed to the SO_2 recovery unit.

Smelting of copper ores is carried out in a reverberatroy furnace at a temperature of approximately 2400°F. In the reverberatory, all of the copper and some of the iron in the charge are converted into sulfides which combine to form the matte phase. Also, the excess iron oxide in the furnace is fluxed with siliceous minerals to form a slag. The principal functions of the reverberatory furnace is to melt down the charge and to form the matte and slag phases which segregate into two layers and are separately removed from the furnace. The slag is sent to a dump area and the matte is forwarded to the converter.

During the melting phase in the reverberatory furnace, up to one-half of the sulfur in the charge is oxidized to sulfur dioxide so that typically the sulfur dioxide content in the furnace offgas is between 0.5 and 5.3 percent. The furnace offgas is passed through waste heat boilers to cool the gas and produce steam which in turn is used to generate electric power for the smelter. The furnace offgas is further cooled by air dilution and the dust is removed in electrostatic precipitators.

The copper converters, which operate in batch mode, are used to oxidize and separate the iron and sulfur from the reverberatory matte. Generally two converters are required for each reverberatory furnace. The charge to the converters is the molten matte formed in the reverberatory furnace together with a silica containing flux. Air is blown into the molten matte oxidizing the ferrous sulfide to sulfur dioxide (which typically is 1.5 to 7.0 percent of the converter flue gas) and ferrous oxide which combines with the silica of the flux to form a slag. The oxidation reaction generates enough heat to maintain the converter temperature at approximately 2250°F, and no fuel is required. The slag is skimmed from the converter and transported back to the reverberatory furnace. At the same time, additional matte is added to the converter, and the process is repeated until a suitable amount of copper sulfide is accumulated. Then air blowing is continued without further matte additions, causing the oxidation of the cuprous sulfide. As an appreciable amount of cuprous oxide forms, it in turn reacts with cuprous sulfide to form blister copper and sulfur dioxide. These reactions continue until practically all of the sulfur has been eliminated.

A converter may take from 8 to 24 hours to complete a cycle. The converter offgas flow rate and sulfur dioxide concentration will vary during an operating cycle but in the smelter model the the assumption is made that by employing several converters an average converter offgas stream can be maintained. The converter offgas is cooled by air dilution and dust is removed by electrostatic precipitators.

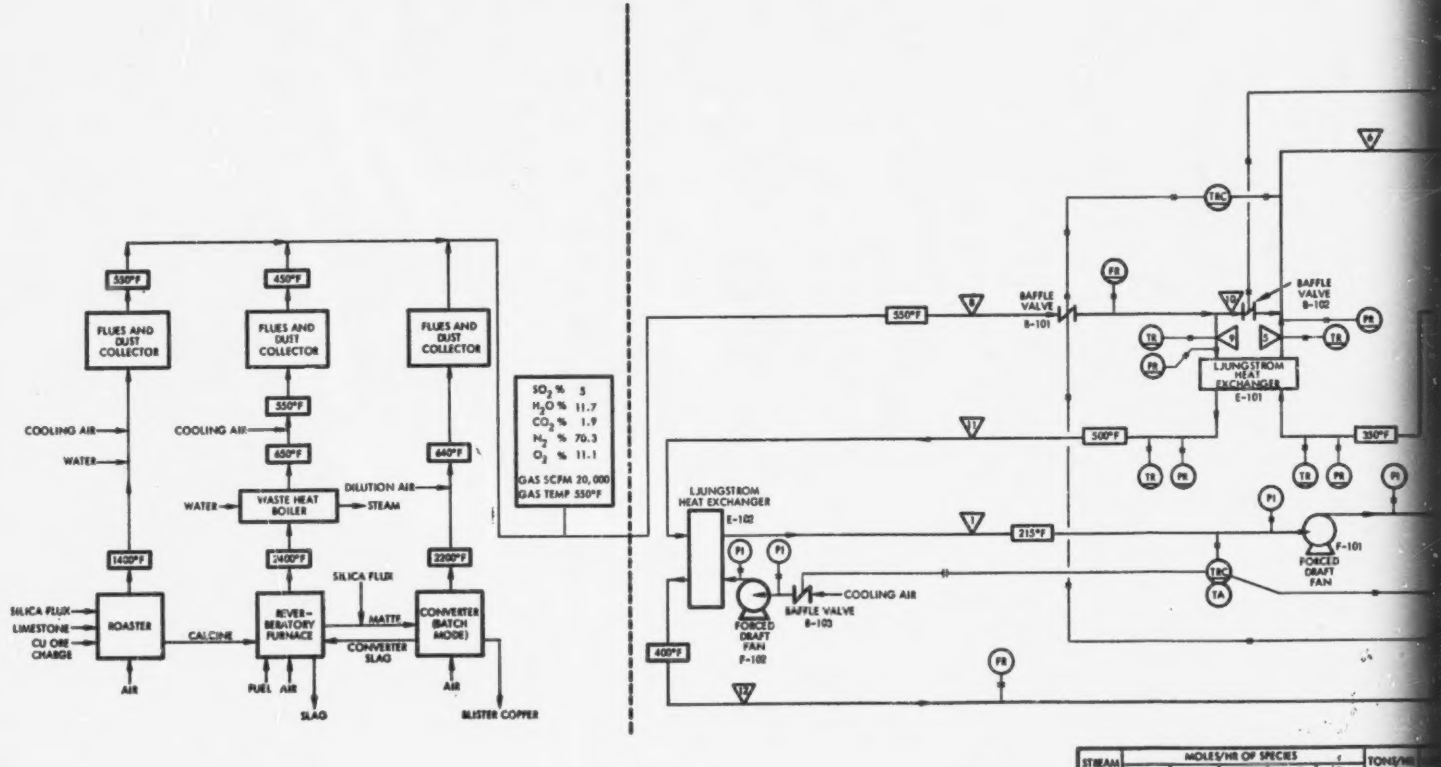
In the new smelter design case, the feed to the SO_2 recovery system is considered to be composite of the flue gas streams from the roaster, reverberatory furnace and converters. In practice, the SO_2 recovery system may be used to treat each of the SO_2 containing flue gas streams individually, if warranted.

5.4.2 Process Design Analysis

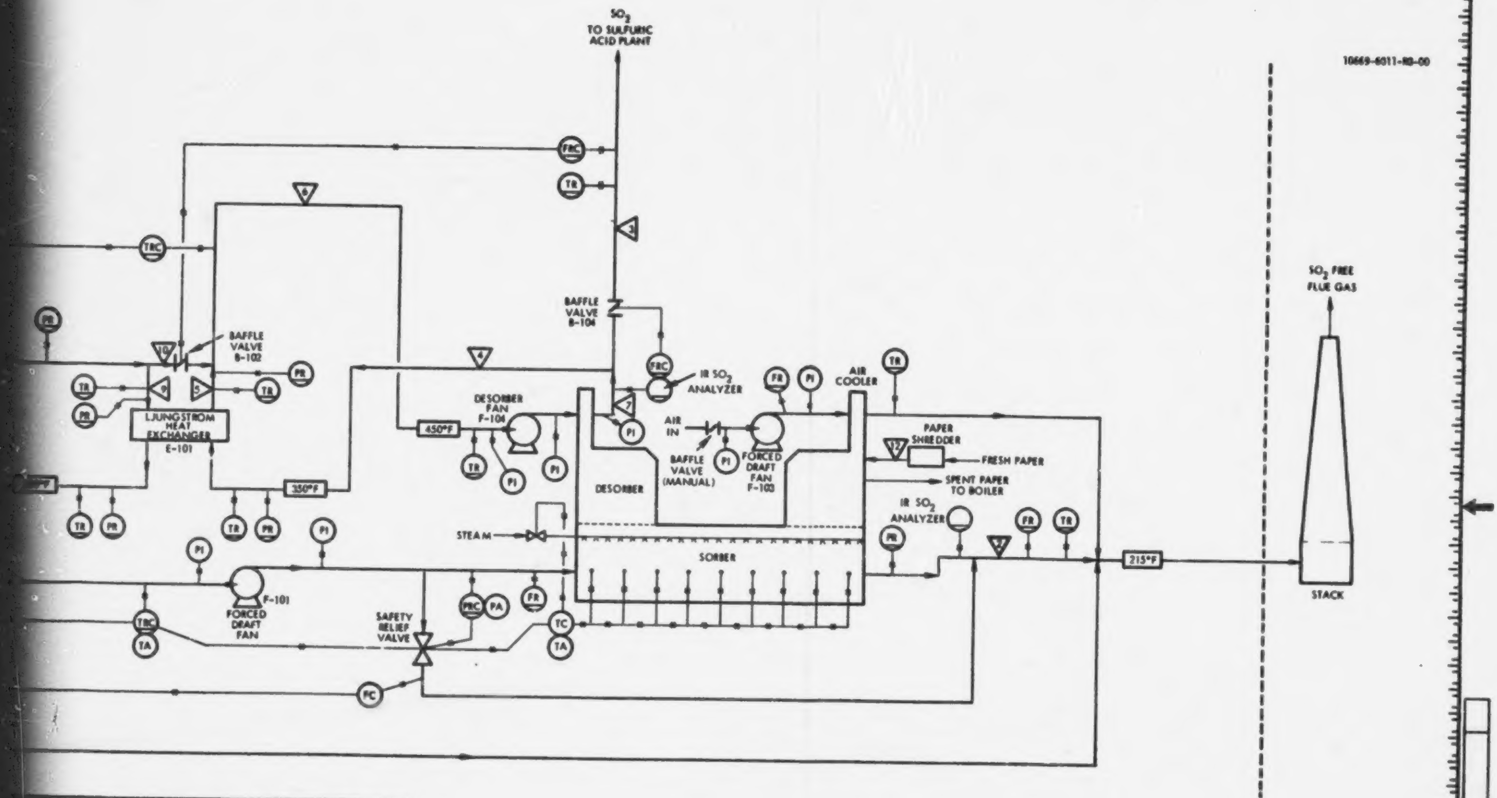
In the new smelter case, the flue gas being fed to the sulfur dioxide recovery system is specified to be 5% sulfur dioxide by volume and having a flow rate of 20,000 SCFM. The temperature of this copper smelter flue gas is designed to be 550°F and the composition is assumed to be (Reference 31):

Component	Volume Percent
SO_2	5.0
N_2	70.3
O_2	11.1
CO_2	1.9
H_2O	11.7

A complete heat and mass balance on the sulfur dioxide recovery system was used to determine the temperatures and flow rates of the different stream, as indicated in the process flowsheet (Figure 20). Since the smelter flue gas already contains a high concentration of SO_2, about half of the hot flue gas in Stream 8 is fed to the recirculating desorption gas stream directly, both to provide the heat required to desorb the SO_2 on paper, and to maintain the level of SO_2 concentration in the exiting stream from the desorption station (Stream 3) at 9 percent. The other half of the hot flue gas in Stream 8 after first heat exchanging with the recirculating desorption gas (Stream 4) and then the cooling air (Stream 12), enters the moving-bed sorber at 215°F, where the suflur dioxide in the flue gas is sorbed on shredded paper packed in baskets on rails moving slowly in the opposite direction. The low SO_2 concentration flue gas (0.5%) leaving the sorber is combined with the hot air (at about 400°F) exiting from Ljungstrom heat exchanger E-102


550°F
450°F
FLUES AND DUST COLLECTOR
FLUES AND DUST COLLECTOR
FLUES AND DUST COLLECTOR
550°F
COOLING AIR
WATER
COOLING AIR
650°F
640°F
DILUTION AIR
WATER
WASTE HEAT BOILER
STEAM
1400°F
2400°F
2200°F
SILICA FLUX
SILICA FLUX
LIMESTONE
CU ORE CHARGE
ROASTER
CALCINE
REVER-BERATORY FURNACE
MATTE
CONVERTER (BATCH MODE)
CONVERTER SLAG
AIR
FUEL
AIR
SLAG
AIR
BLISTER COPPER
SO_2 % 5
H_2O % 11.7
CO_2 % 1.9
N_2 % 70.3
O_2 % 11.1
GAS SCFM 20,000
GAS TEMP 550°F
6
TRC
FR
550°F
8
BAFFLE VALVE
B-101
10
BAFFLE VALVE
B-102
PR
TR
9
5
TR
PR
LJUNGSTROM HEAT EXCHANGER
E-101
11
500°F
350°F
TR
PR
TR
PR
PI
PI
LJUNGSTROM HEAT EXCHANGER
E-102
1
215°F
PI
PI
F-101
FORCED DRAFT FAN
TRC
TA
COOLING AIR
BAFFLE VALVE
B-103
FORCED DRAFT FAN
F-102
400°F
FR
12

STREAM NO.	MOLES/HR OF SPECIES					TONS/HR PAPER
	SO_2	N_2	CO_2	H_2O	O_2	
1	78	1,100	30	183	173	
2	7	1,100	30	183	173	
3	152	1,132	31	189	179	
4	201	1,301	40	251	238	
5	205	1,560	42	261	247	
6	292	2,632	71	440	417	
7	353	2,632	71	440	417	
8	159	2,232	60	372	352	
9	82	1,160	31	193	182	
10	77	1,072	29	179	170	
11	78	1,100	30	183	173	
12	—	1,116	—	—	297	
13	—	—	—	—		1.28


SO_2
TO SULFURIC ACID PLANT
10669-6011-RB-00
FRC
TR
TRC
PR
BAFFLE VALVE B-102
10
9
5
6
4
3
TR
PR
LJUNGSTROM HEAT EXCHANGER
E-101
450°F
350°F
DESORBER FAN F-104
BAFFLE VALVE B-104
IR SO_2 ANALYZER
7
PI
AIR IN
BAFFLE VALVE (MANUAL)
FORCED DRAFT FAN F-103
FR
AIR COOLER
PAPER SHREDDER
12
FRESH PAPER
SPENT PAPER TO BOILER
DESORBER
STEAM
SORBER
IR SO_2 ANALYZER
11
215°F
SO_2 FREE FLUE GAS
STACK
F-101
FORCED DRAFT FAN
SAFETY RELIEF VALVE
PRC
PA
TC
TA
FC

	MOLES/HR OF SPECIES					TONS/HR PAPER	MM BTU/HR H - H 298°K
	SO_2	N_2	CO_2	H_2O	O_2		
	78	1,100	30	183	173		1.66
	7	1,100	30	183	173		1.39
	152	1,132	31	189	179		3.75
	201	1,501	40	251	238		4.97
	205	1,560	42	261	247		5.90
	282	2,632	71	440	417		11.66
	253	2,632	71	440	417		8.72
	157	2,232	60	372	351		11.97
	82	1,160	31	193	182		6.21
	77	1,072	29	179	170		5.76
	78	1,100	30	183	173		5.28
	—	1,116	—	—	297		0.02
	—	—	—	—		1.23	—

KEY FOR INSTRUMENTATION

○	MOUNTED LOCALLY
⊖	MOUNTED IN CONTROL ROOM
FR	FLOW RECORDER
FRC	FLOW RECORDER CONTROLLER
PA	PRESSURE ALARM
PI	PRESSURE INDICATOR
PR	PRESSURE RECORDER
PRC	PRESSURE RECORDER CONTROLLER
TA	TEMPERATURE ALARM
TC	TEMPERATURE CONTROLLER
TI	TEMPERATURE INDICATOR
TR	TEMPERATURE RECORDER
TRC	TEMPERATURE RECORDER CONTROLLER

TRW
ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

Figure 20

NEW SMELTER FLOW DIAGRAM

SIZE D
CODE IDENT NO. 11982
SCALE
SHEET

(Stream 12) and from the air cooling station to give additional thermal life to the stack gases. The method of desorption for the smelter case is identical to that described in the power plant cases.

The volume of smelter flue gas is relatively small when compared to the power plant cases and consequently the pressure drop across the sorber is no longer a determining factor in the design of the system. However, there is an additional parameter, namely the sulfur dioxide concentration in the exiting stream from the desorption station, that does effect the size of the sorption unit. In the design case, the sulfur dioxide concentration in the feed stream to the sulfuric acid facility (Stream 3) is maintained at 9 percent and consequently only about half of the initial flue gas stream enters the sorber. (If this concentration level were to be lowered, substantially less than half of the flue gas would have to be treated in the sorption unit.) An economic advantage does result if the feed stream to a sulfuric acid plant is concentrated from 5% to 9% SO_2, as shown in Figure 21 , and it should also be noted that little advantage is gained if the sulfur dioxide concentration is increased about 9 percent (Reference 32).

Another parameter which determines the design of the sorption unit is the amount of sulfur dioxide on the paper leaving the sorber (Figure 22). In the design case, the sulfur dioxide content of the paper was set at 0.018 lbs SO_2 per lb paper. This value was determined under the assumption that the equilibrium constant, H, described in Section 3, dictates the sulfur dioxide equilibrium capacity of the paper which for this case is calculated at 0.021 lbs SO_2/lb paper based on the flue gas SO_2 concentration of 5 volume percent.

The process mathematical model was used to arrive at a design in which the sorber has a cross-sectional area of 144 square feet and a length of 105 feet. The estimated pressure drop across the sorber using Ergun's equation (Equation 10) is 2.5 inches H_2O. Other design parameters which pertain to the sulfur dioxide recovery process for a new smelter are:

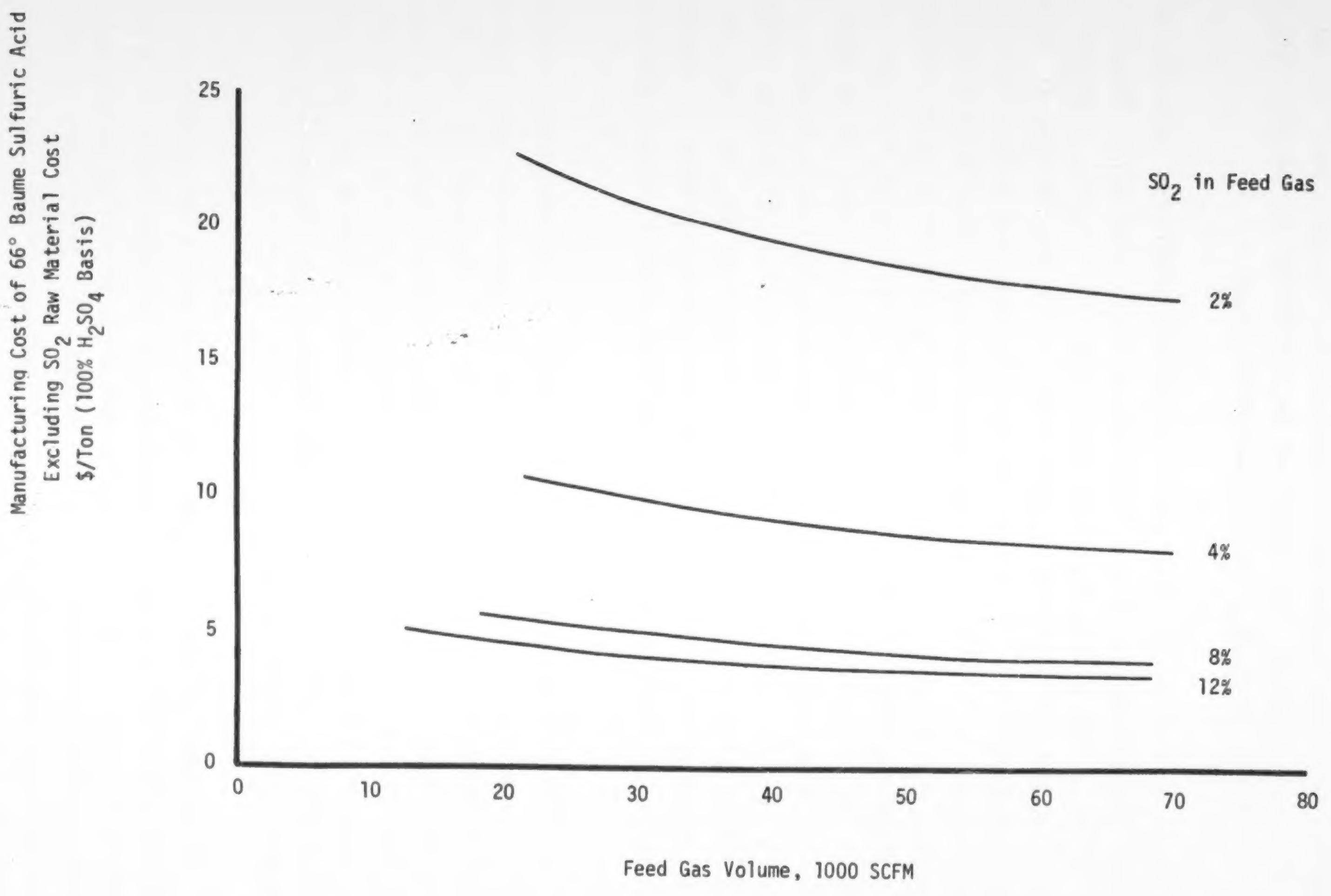


Figure 21. Manufacturing Cost of Sulfuric Acid vs. Feed Gas Volume

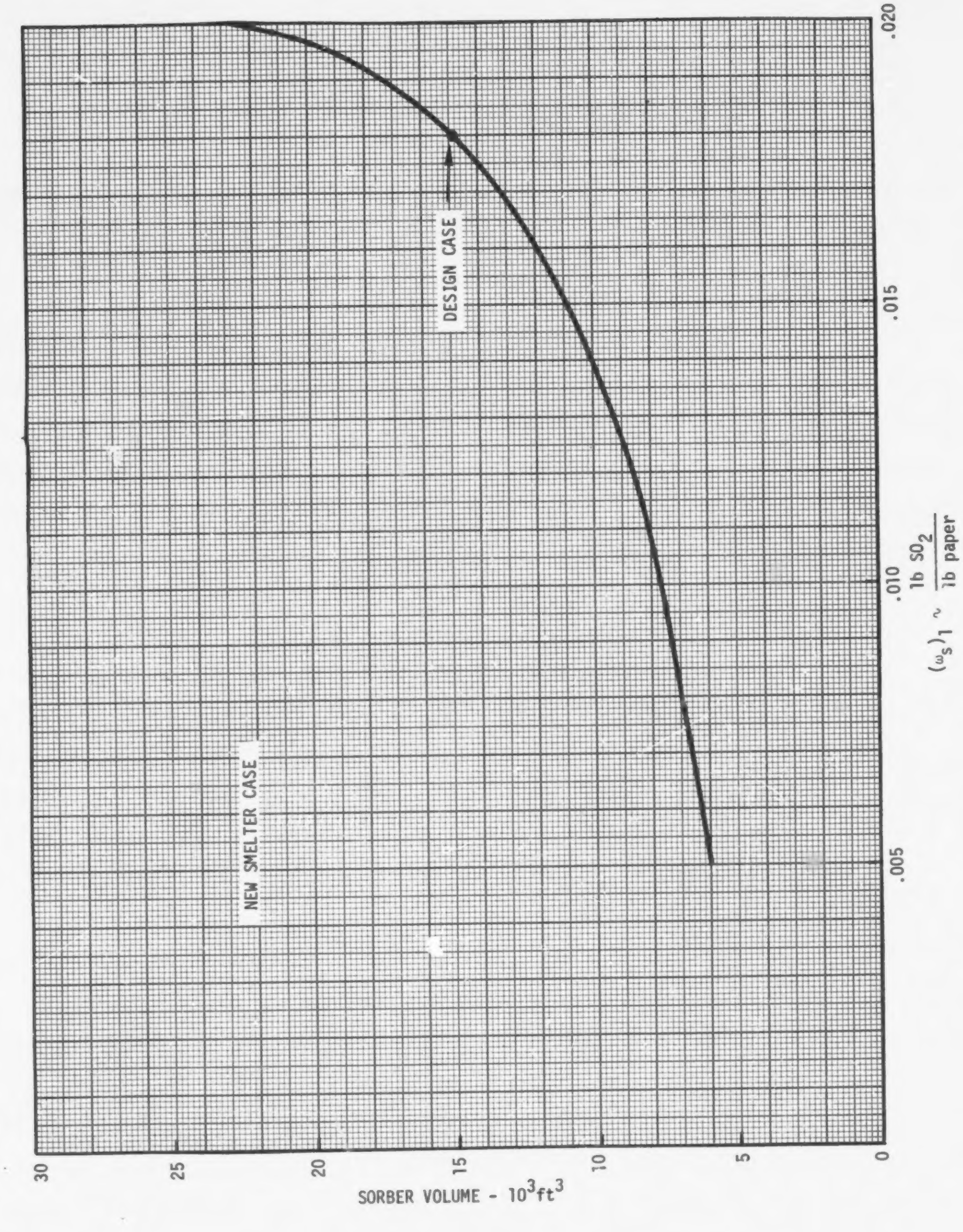


Figure 22. Mass Fraction of SO_2 on Paper Exiting from Sorber vs. Volume of Sorber

- Total weight of the paper packing in the sorber is 53 tons
- The paper replacement rate is 1 percent by weight each cycle through the sorber
- Void fraction of the sorber is 0.9
- Velocity of the paper bed is 4.1 ft/min
- Velocity of the flue gas in the sorber is 100 ft/min

The mass fraction of sulfur dioxide in the flue gas and on the paper as a function of distance along the sorber is presented in Figure 23.

5.4.3 Economic Analysis

The results of the economic analysis for the new smelter case estimate that the sulfur dioxide recovery process will require a capital investment of $386K and will have an equipment operating cost of $2 per hour (Table IX). The total cost breakdown for the process indicates that an operating profit of $3.80 per hour can be realized (Table X). The cost consideration used in the economic analysis are presented below:

(1) The superstructure of the sorber/desorber system is constructed of reinforced concrete. The foundation concrete poured to a depth of 5 feet is costed at $55 per cubic yard of concrete; the wall concrete, an average of 2/3 foot thick, is costed at $115 per cubic yard; and the prestressed concrete roof, an average of 1 foot thick, costs $185 per cubic yard (Reference 9). Twelve concrete support buttresses cost $4.8K.

(2) The structural steel used in the construction of the sorber system and the "paper" basket network is costed as being equivalent to a single story office building. The structural steel is priced at $350/ton (Reference 10). The sorber system is insulated against heat losses at a cost of $2 per square foot of surface area.

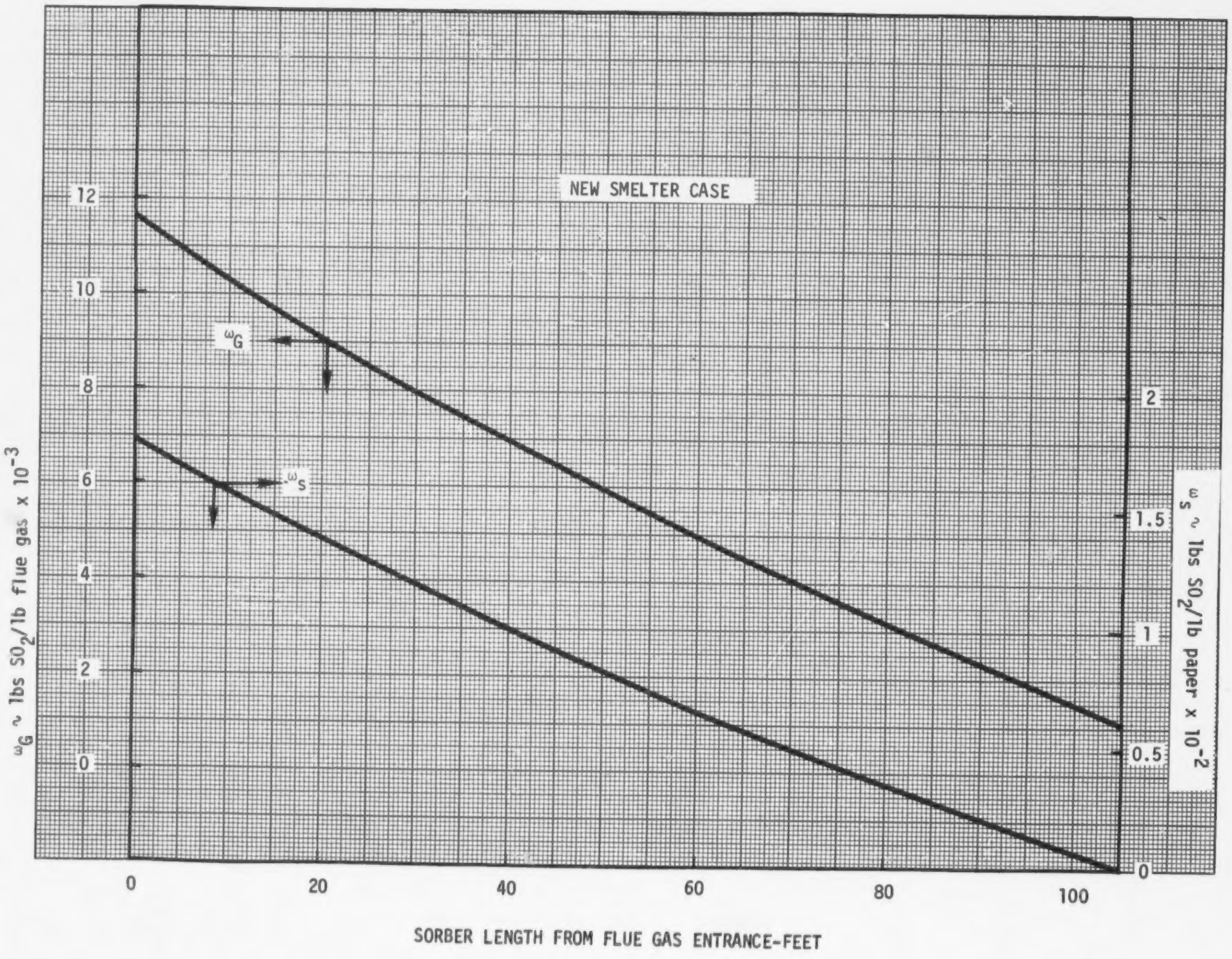


Figure 23. Mass Fraction of SO_2 on Paper Exiting from Sorber vs. Volume of Sorber

TABLE IX

EQUIPMENT AND OPERATING COST BREAKDOWN

NEW SMELTER CASE

	Installed Capital Costs ($000)		Operating Costs ($/hr)
Sorber/Desorber Structure	78		
Structural Steel		7	
Reinforced Concrete		58.5	
Insulation		12.5	
Paper Transporter System	27		
Basket and Rail System		17.5	
Electric Motors		9.5	0.75
Fans	72		
Sorber Forced Draft (F-101)		11	0.25
Air Cooling Forced Draft (F-102)		9	0.25
Air Cooling Forced Draft (F-103)		21	0.25
Desorber Fan (F-104)		31	0.35
Heat Exchangers	53		
Ljungstrom (E-101)		18	
Ljungstrom (E-102)		35	
Ducts	97		
Sorber Inlet		23	
Sorber Outlet		23	
Desorber		32	
Air Cooler		18	
Sorber By-Pass		1	
Baffle Valves	2		
Smelter Flue Main (B-101)		0.4	
Desorber Make-up (B-102)		0.4	
Cooling Air (B-103)		0.6	
SO_2 Product (B-104)		0.6	
Steam Quench System		8	
Instrumentation		30	
Paper Storage		3	
Paper Conveyor		10	0.10
Paper Shredder		6	0.05
TOTAL		386	2.00

TABLE X
SULFUR DIOXIDE RECOVERY PROCESS COST BREAKDOWN
NEW SMELTER CASE

		($/hr)
Expenses:		
Equipment Operating Costs		2.00
Paper Replacement Cost		7.50
Depreciation (10-Year Straight-Line)		4.90
Maintenance (5% of Capital Investment Per Year)		2.40
Insurance (1% of Capital Investment Per Year)		0.50
Financing Interest (7% of Capital Investment Per Year)		3.40
Taxes (2% of Capital Investment Per Year)		1.00
Labor with 100% Overhead (2 Operators Per Shift)		25.00
	Subtotal	46.70
Credits:		
SO_2 as Feed Stream In Sulfuric Acid Manufacture (@ $10/Ton SO_2)		45.70
Spent Paper as Fuel		4.80
	Subtotal	50.50
	Total Operating Profit	3.80

(3) The paper transport system includes support rails, steel mesh baskets and electrically powered drivers. The steel required is costed as being equivalent to the structural steel needed in the sorber. A 100 HP motor is used to drive the transport system.

(4) The forced draft fan (F-101) needed to compensate for the pressure drop in the sorber is sized at 40 HP. The installed capital cost is estimated at $11K (Reference 19). The two air cooling fans, (F-102) and (F-103) and the desorber fan (F-104) are sized at 40 HP, 80 HP and 80 HP respectively.

(5) Heat exchangers E-101 and E-102 are costed as Ljungstrom regenerative models.

(6) The sizing of the duct work is based on a gas velocity of 2000 ft/min. The ducting is fabricated from 10 gauge Corten steel and has an average weight of 7-1/2 lbs per ft^2 and is insulated where necessary. The duct material is costed at 60¢/lb with an added 50¢/lb for installation (References 22 and 23). The duct work includes 400 feet leading to and from the sorber, and 200 feet each in the desorption and air cooling sections.

(7) The sulfur dioxide recovery system depreciated at 10 percent of capital per year. Maintenance, taxes, insurance, etc., amount to an additional 10 percent of capital per year.

(8) The paper replacement rate is 1 percent by weight each cycle through the sorber or 1.25 tons/hr. The waste paper is costed at $6/ton. Heat from the combustion of spent paper is credited at 25¢/MM Btu.

(9) The concentrated (9 percent) sulfur dioxide stream is credited at \$10/ton SO_2 as a feed stream to a sulfuric acid facility (corresponds to \$15/ton sulfuric acid). The effect of the sulfur dioxide byproduct credit on the total operating cost of the process is shown in Figure 5.18.

(10) The smelter operates 330 days per year. The sulfur dioxide recovery unit requires 2 operating positions at a cost of \$100,000 per position per year.

(11) Electrical power is costed at 0.5¢/KWH.

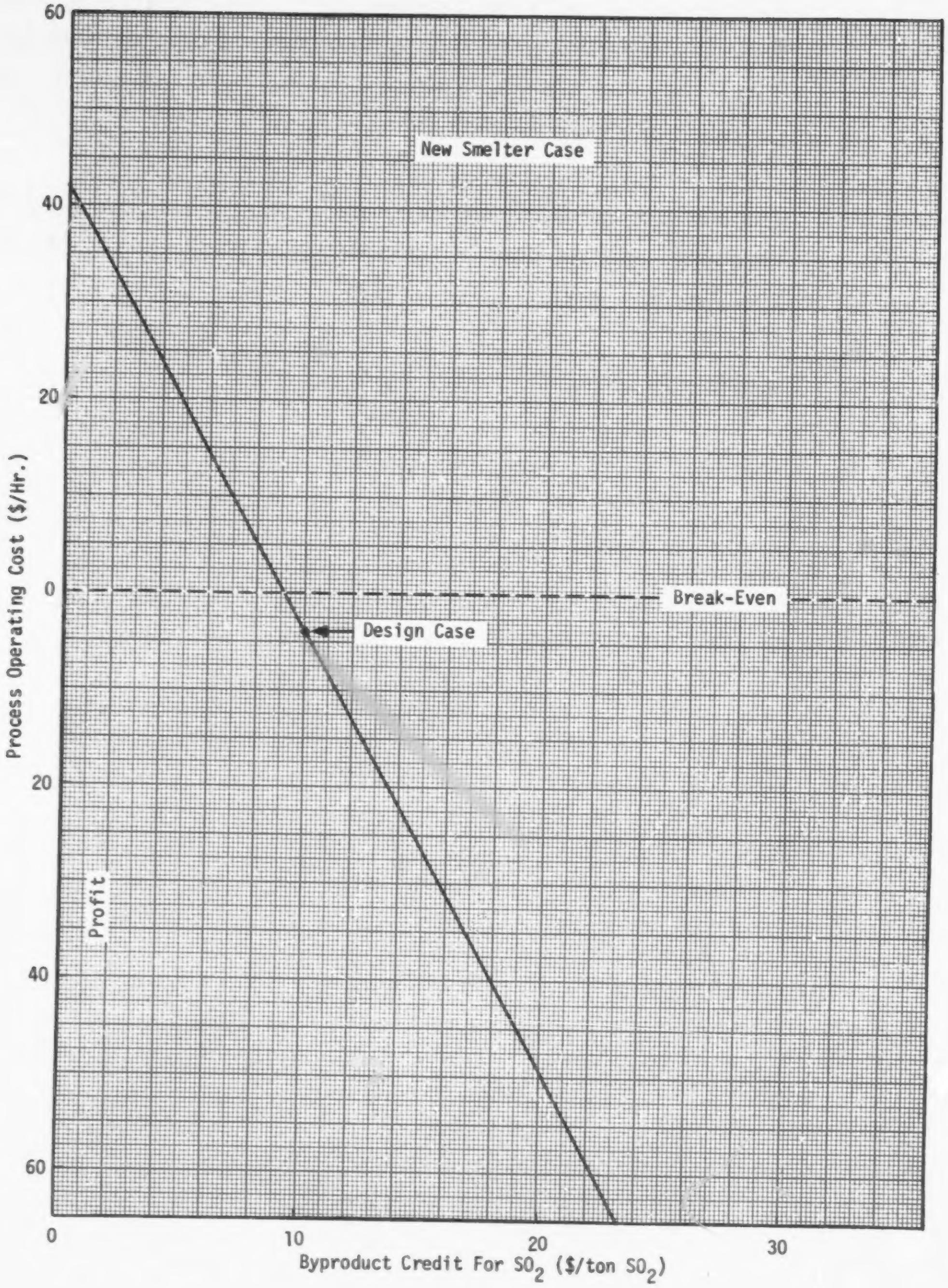


Figure 24. Effect of SO_2 Byrpoduct Credit on the Operating Cost of the SO_2 Recovery Process

6.0 PROCESS SAFETY

No major stability problems or hazardous situations were identified in the design analysis of the sulfur dioxide process. To insure safe operation and also to protect the equipment and paper sorbent from possible costly damage, several safety systems are built into the process. One such system monitors the temperature of the flue gas entering the sorber and if it exceeds a preset limit, an alarm sounds and an automatic controller opens a relief valve causing the flue gas to bypass the sorber. An extension of this system monitors temperatures throughout the sorber system, and if a "hot" temperature is detected, the alarm sounds, the sorber bypass valve opens and the automatic controller activates a steam quench system to quickly extinguish any fires in the sorber/desorber system. This system provides protection against fires in the sorber and also against temperature upsets in the flue gas generating device.

A pressure monitoring system guards against another potential problem, a pressure buildup in the sorber because of blockage of the flue gas path. If an increase in the pressure of the sorber is detected, an automatic controller opens the sorber bypass valve and the flue gas stream is diverted to the stacks. In all the design cases, the sorber void fraction is high (0.9) and the paper packing is specified to be thin strips in order to avoid "plugs" as much as possible.

The above described safety systems require that a safety relief valve be opened to divert the flue gas stream around the sorbers whenever a potential hazard occurs. One design concept for this safety relief valve is a hydraulic valve as depicted in Figure 25 . During normal operation of the sorber, a fluid (probably water) is pumped into the baffled reservoir of the sorber bypass duct, and the flue gas flow is cut off in the bypass line and directed into the sorber. When a safety hazard is detected, the automatic controller activates the pumps and the fluid is quickly drained from the bypass duct reservoir and pumped into a similar reservoir in the sorber feed duct. Another design concept for the safety relief valve

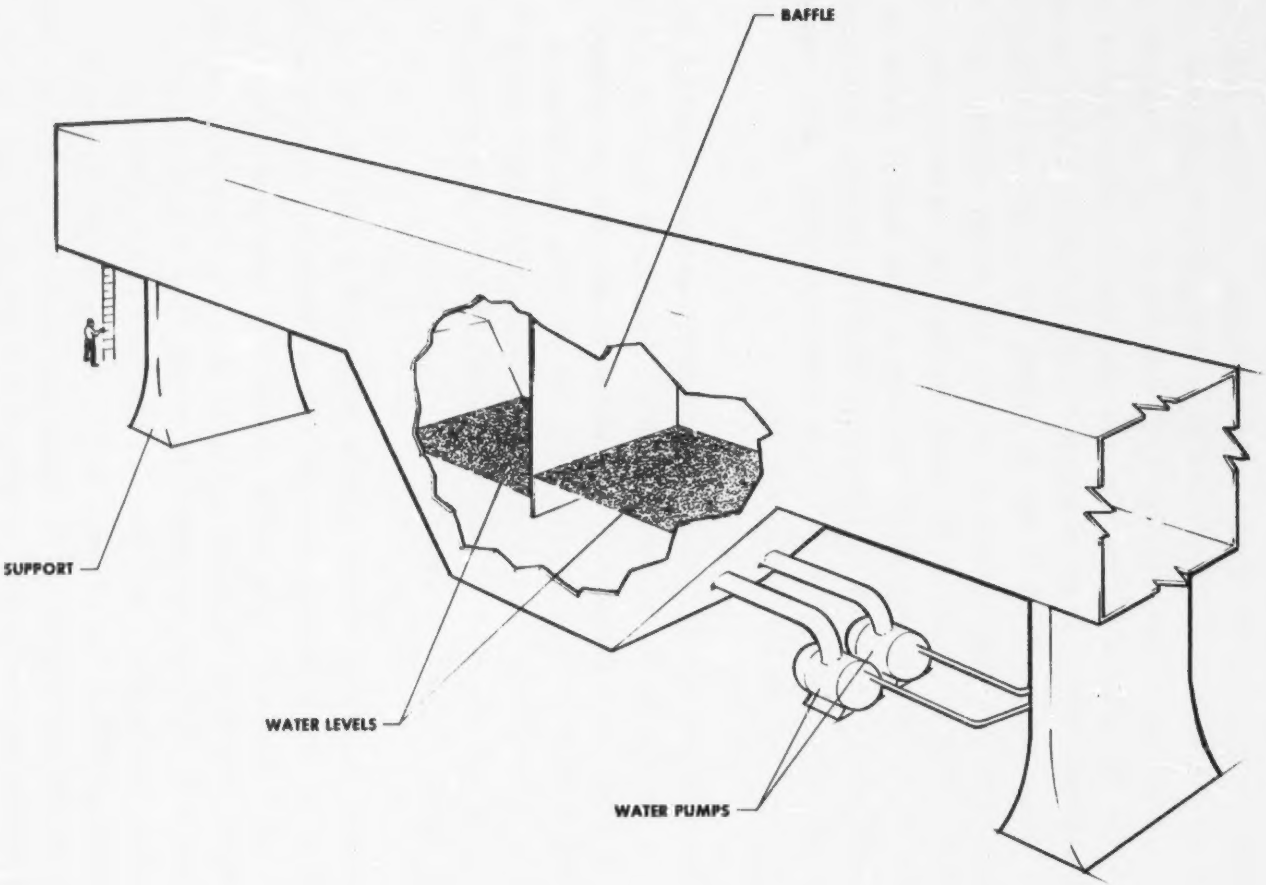

BAFFLE
SUPPORT
WATER LEVELS
WATER PUMPS

Figure 25. Hydraulic Valve for Controlling Gas Flow

employs a flexible bladder, which can be inflated by filing with a fluid, to cut off the flue gas flow.

Finally, it can be noted that problems such as a boiler tube rupture, which would send a large amount of steam and water into the system, should not cause any serious damage to the equipment or the paper packing. Along a similar line, an oxygen deficiency in the boiler or a failure of the dust collectors, resulting in large amounts of carbon entering the sulfur dioxide recovery system, should not adversely affect the operation of the sorber and, in fact, the paper would entrain the solid particles in the flue gas.

7.0 CONCLUSIONS AND RECOMMENDATIONS

The results of the sulfur dioxide removal and recovery process design and economic evaluation demonstrate that the proposed cellulosic sorbent system could be feasible for the four applications considered if the process assumptions prove to be correct. It is particularly import, for example, that the paper be regenerable several hundred times or the process economics become poor.

	Capital Cost ($000)	Operating Cost	
		($/Hr)	($/Ton Coal)
Large New Power Plant Case	12.8	147	0.31
Large Existing Power Plant Case	13.6-17.6	168-257	0.35-0.54
Small Existing Power Plant Case	3.7-4.2	77-89	0.77-0.89
New Smelter Case	0.4	3.80 (Profit)	---

The costs for the power plant cases compare favorably with those estimated for other proposed sulfur dioxide recovery processes (Reference 33):

	Operating Cost ($/Ton Coal)
Reinluft acitivated char*	2.45
Bureau of Mines alkalized alumina*	1.54
Monsanto catalytic oxidation*	1.75
TRW waste cellulosic**	0.88

---

*Operating cost is based on a new 800 MW power plant and includes capital charges of 14% of total investment but excludes byproduct credit.

**Operating cost is based on a new 1100 MW power plant and includes capital charges of 13% of total investment but excludes byproduct credit.

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The sulfur dioxide recovery unit for the new smelter case is more economically attractive than the other cases. With no SO_2 byproduct credit, the recovery process could have an operating cost of $42 per hour and with a $10/ton credit for the SO_2, the process shows a profit of $3.80 per hour.

Since the sulfur dioxide recovery process does appear economically feasible, the next phase in the development of the process should include a laboratory scale test program to identify an optimum operating range and then pilot plant testing on an actual flue gas stream for an extended period of time. The design and economic evaluation did identify several parameters in the process which, because of their significant economic effect, warrant further laboratory study. One such parameter is the SO_2 sorption rate of the paper itself. It may be possible that pretreating the paper before it enters the sorber, for instance, to increase its surface area, can cause the sulfur dioxide sorption rate to be significantly increased and consequently bring about a reduction in the size and the cost of the needed equipment.

Another area which should undergo evaluation is the degradation rate of the paper sorbent. Again possibly by pretreating the paper, the sorbent degradation rate can be greatly reduced.

The heat requirements during desorption should be studied on both a laboratory and a pilot plant scale to determine an optimum contact time between hot flue gas in the desorber and the paper. The economics of the process are closely tied to the degree in which the sulfur dioxide can be removed from the paper and the amount of heat that is required for desorption.

The indicated laboratory studies should be followed by pilot plant testing. Here materials of construction should be further evaluated and long-term operating stability should be verified. At the same time, methods of handling the paper both at its initial collection point and also at the process site should be devised.

Finally, throughout the laboratory and pilot scale testing, the process economics must be upgraded regularly to include the effects of any new findings and also critically reviewed at regular intervals to assure that the process retains its competitiveness.

8.0 PATENT APPLICATIONS

A patent application covering the use of cellulosics, including waste paper, as a means of removing and recovering sulfur dioxide from flue gas streams was filed with the United States Patent Office by TRW. Also, two invention disclosures pertaining to methods of controlling flue gas flow were submitted to the TRW Patent Department.

One disclosure (Docket No. 5268) pertains to a hydraulic valve for regulating high-volume gas flows. The hydraulic valve system includes a baffled reservoir located in the gas duct and a pumping system that can quickly fill and drain the reservoir of liquid (normally water). A practical application of the hydraulic valve is discussed in Section 6.

The other invention disclosure (Docket No. 5270) relates to an inflatable bladder valve for regulating fluid flow. In the operation of the bladder valve, a gas or liquid is pumped into or out of a flexible bladder located within the flue gas duct causing the bladder to expand or deflate thereby controlling the fluid flow.

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APPENDIX A

END PRODUCTS FROM RECOVERED SULFUR DIOXIDE

The proposed process for removing SO_2 from flue gases using newsprint as sorbent provides SO_2 recovery readily convertible to commercially unable forms. Unlike several other SO_2 recovery processes, the end product of this process could be either pure concentrated sulfuric acid or elemental sulfur. In general, because of the higher freight costs for the sulfuric acid, the preference of one end product over the other will depend by and large on the local demand for the acid. The large quantity of concentrated sulfuric acid that could be produced from one single power plant (438,000 tons acid per year for a 1100 MW plant with 0.3% SO_2 in the pretreated flue gas stream), however, indicate that in most cases, elemental sulfur is the favored form of end product. And, although the sulfur requirements for the United States is growing at a rate of over 10% per year (a major portion of the demand is for sulfuric acid utilized in the production of phosphate fertilizers), oversupply of sulfur due to efficient SO_2 recovery methods is expected in the future. The credit taken for sulfuric acid or elemental sulfur will therefore be a decreasingly important factor in both the choice of the SO_2 removal process and the SO_2 end product. Included here are brief descriptions of the sulfuric acid and elemental sulfur processes from sulfur dioxide.

A.1 SULFURIC ACID

The gas stream from the desorber, containing 9 percent sulfur dioxide, is mixed with air to provide enough oxygen to leave an excess of 5 percent free oxygen after reaction (Figure A-1). The process stream is then dried in a drying tower to lower the water concentration to less than .01 gram H_2O/cubic foot of gas. The drying tower is a packed column with concentrated sulfuric acid flowing countercurrent to the gas stream.

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After drying, the desorber stream is passed through a mist precipitator (Stream 5) to remove any sulfuric acid mist that may have formed and is split into two streams. The main stream (Stream 7) prior to being fed to the first stage of the converter is heated to the reaction temperature of 860°F by heat exchange with the streams leaving the second and fourth stages of the converter. The remaining portion of the desorption stream (Stream 6) is injected prior to the second stage of the converter in order to control the temperature in that stage. The converter is a four-stage column packed with either vanadium or platinum catalyst on a suppor material.

The stream leaving the second stage of the converter (Stream 10) is heat exchanged with the incoming desorber gas stream to keep the temperature within the reaction range in the third stage of the converter. As the temperature increases, the conversion of SO_2 to SO_3 decreases but the rate of reaction increases. Therefore, the temperature in the first stage of the converter is 860°F for a fast reaction rate, and decreases through the following stages to increase the conversion. At the end of the third stage, the gas is withdrawn (Stream 14) and cooled by heat exchange before being fed to the intermediate absorption tower. At this stage, the SO_2 has reached a point of about 90% conversion to SO_3.

The intermediate absorption tower, a packed column with 98% sulfuric acid flowing countercurrent to the process stream absorber, absorbs all of the SO_3 contained in the feed stream (Stream 15). The stream existing from the top of the intermediate absorber which now has a SO_2 concentration of 0.7 to 1.0% is heat exchanged with the process stream from the third stage of the converter to raise its temperature to 770°F and is then fed into the fourth stage of the converter where virtually all of the remaining SO_2 is converted to SO_3.

The output stream from the fourth stage of the converter (Stream 12) is heat exchanged with the incoming flue gas stream and is fed to the final absorption tower where the SO_3 is absorbed into 98% sulfuric acid. The overall conversion of SO_2 to sulfuric acid is 99.6 to 99.8%.

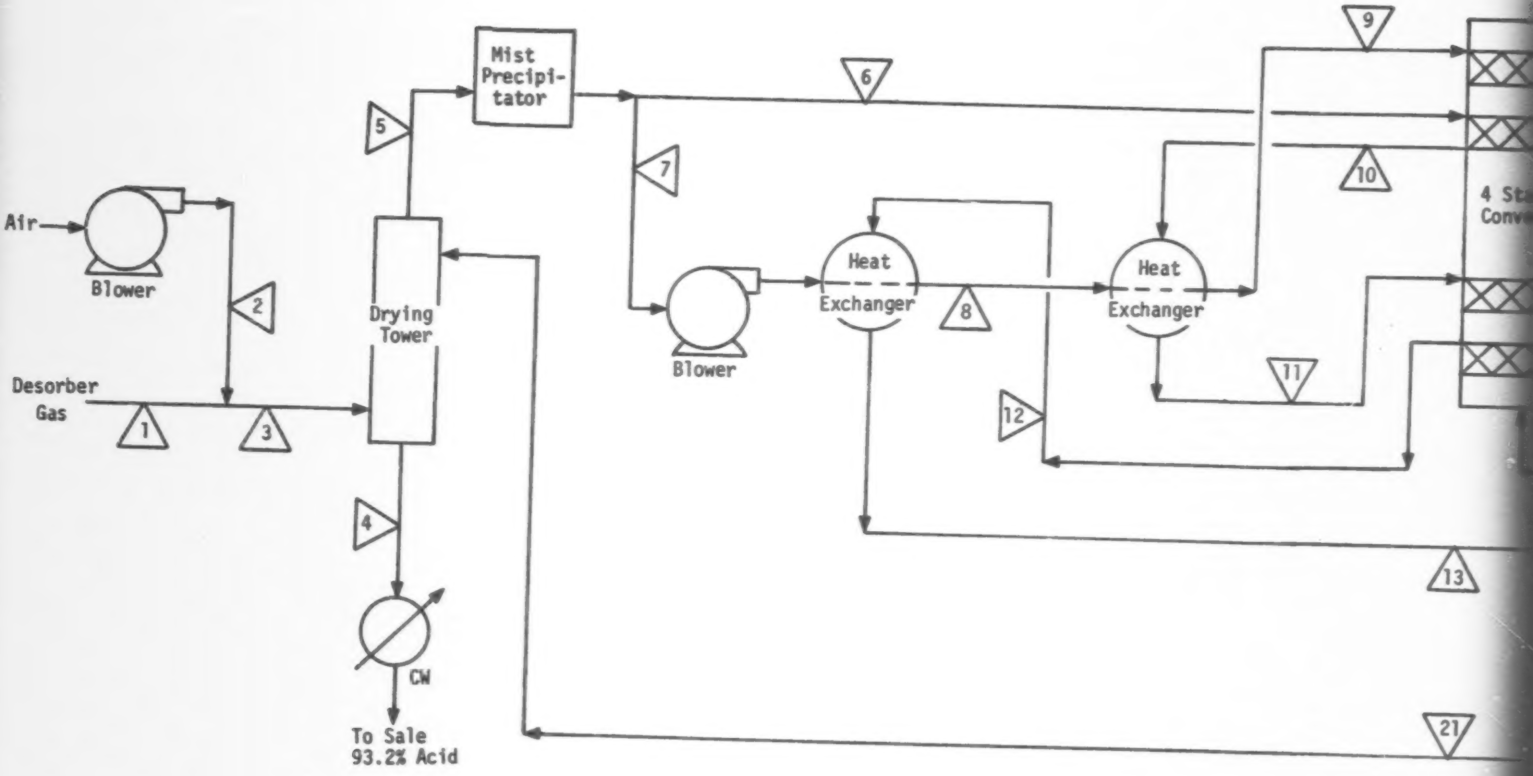
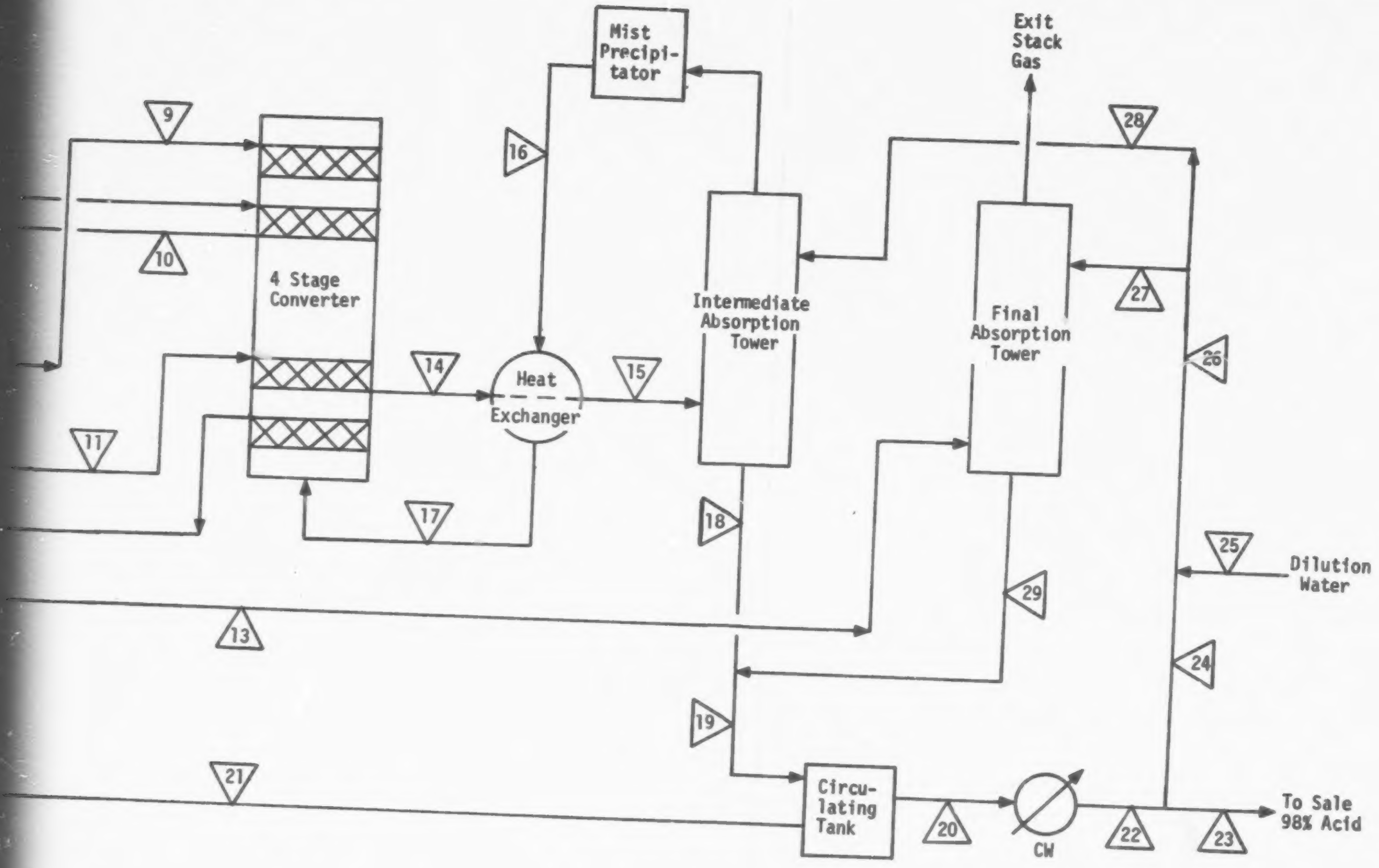

Air
Blower
2
Desorber Gas
1
3
Drying Tower
5
4
CW
To Sale 93.2% Acid
Mist Precipi-tator
6
7
Blower
Heat Exchanger
8
Heat Exchanger
9
10
11
12
13
21
4 Sta
Conv

FIGURE 4-1. SULFURIC ACID PROCESS DIA


Mist Precipi-tator
Exit Stack Gas
9
16
28
10
4 Stage Converter
Intermediate Absorption Tower
Final Absorption Tower
27
26
14
Heat Exchanger
15
11
17
18
25
Dilution Water
29
13
24
19
21
Circu-lating Tank
20
CW
22
23
To Sale 98% Acid

1. SULFURIC ACID PROCESS DIAGRAM

The strong sulfuric acid used to absorb the SO_3 is diluted with water or weak acid to keep the concentration constant in the absorbers. The acid leaving the absorbers is cooled and some is recirculated to the absorption towers while the rest is piped to storage for sale (References 34 and 35).

A sulfuric acid plant similar to the one described above with a capacity of 550 tons/day would require a capital investment of approximately 1.7 MM dollars.

A.2 ELEMENTAL SULFUR

One alternative byproduct that could be obtained from the desorbed sulfur dioxide stream is elemental sulfur. This would require conversion of two-thirds of the sulfur dioxide in the desorbed stream to hydrogen sulfide and then reacting the hydrogen sulfide and remaining sulfur dioxide in a Claus unit to obtain elemental sulfur.

The sulfur dioxide could be converted to hydrogen sulfide by a reaction with a reducing gas. The reducing gas could be obtained by reacting steam with coal or methane. In this process, the reaction producing the reducing gas occurs at 1500 to 1800°F while the hydrogen sulfide-sulfur dioxide reaction takes place at 500°F.

There is a large amount of heat liberated during the hydrogen sulfide-sulfur dioxide reaction which can be converted into steam. The steam credit compensates for the steam used in the production of the reducing gas and eliminates most of the utility operating costs.

APPENDIX B

FIXED BED OPERATION

During Phase II of the program, the initial process design for the SO_2 removal system consisted of two fixed-bed sorbers, - one operating in the SO_2 sorption mode, and another undergoing regeneration of the paper and recovery of the SO_2 by thermal desorption. A mathematical model was subsequently developed to simulate the unsteady-state sorption of SO_2 on the paper. The SO_2 concentration in the flue gas and on the paper as functions of time and distance along the sorber could then be obtained from this model by numerical solution of the partial differential equations. Using the experimental results from Phase II of the program as inputs to the model, the preliminary sorber system design for the large new 1100 megawatt power plant case was to consist of two horizontal conduits with dimensions of 100 feet in diameter and 500 feet in length. This initial sorber design, however, was based on the sorption mode batch time only, assuming that the regeneration mode would have a smaller batch time.

The initial concept of the regeneration mode involved recirculating a volume of hot flue gas at 450°F through the sorber to remove the SO_2 on the paper, followed by cooling the paper bed back to the sorption temperature (215°F) with air which then enters the air preheater. The fixed volume of reducing gas is reheated to 450°F after each pass through the sorber by heat exchanging with hot flue gas leaving the economizer, and is recirculated until its SO_2 concentration reaches a minimum level of 9% - suitable for catalytic oxidation to SO_2 and subsequent manufacture of sulfuric acid. To simulate the SO_2 desorption on paper in the fixed-bed sorber, a mathematical model was developed based on a desorption temperature of 400°F. A heat balance on the paper in a differential element of the sorber resulted in the following equation:

$$\frac{\partial}{\partial t}\left(s_s \rho_s T_s\right) = h\left(T_G - T_s\right) \qquad \text{(B-1)}$$

where

s_s = heat capacity of the paper, (Btu/°R-lb. paper).

ρ_s = density of paper, (lb./cu. ft. paper).

T_s = temperature of the paper, (°R).

h = convective heat transfer coefficient from the hot reducing gas to the paper, (Btu/hr-ft^3 paper).

T_G = temperature of the hot reducing gas, (°R).

t = time, (hr.)

A heat balance on both the paper and the reducing gas in a differential element of the sorber resulted in a second equation:

$$\frac{\partial}{\partial t}\left[s_G \rho_G \varepsilon T_G + s_s \rho_s (1 - \varepsilon) T_s\right] = - \frac{\partial}{\partial Z}\left(s_G G T_G\right) \qquad \text{(B-2)}$$

where

ε = void fraction of sorber, (ft^3 actual volume/ft^3 empty sorber).

s_G = heat capacity of the reducing gas, (Btu/°R-lb gas).

ρ_G = density of the reducing gas, (lb./cu. ft.).

G = superficial mass gas velocity, (lb-gas/hr-ft^2 empty cross section).

Z = distance along the sorber, (ft.).

The boundary conditions are:

$$T_s(Z,0) = 675 \text{ (°R)} \qquad \text{(B-3a)}$$

and

at Z = 0

$$s_s \rho_s \frac{\partial T_s}{\partial t} = h\,(910 - T_s) \qquad \text{(B-3b)}$$

which integrates to

$$T_s(0,t) = 910\text{-}235\ e^{-\frac{h}{s_s\rho_s}t} \qquad \text{(B-3c)}$$

Noting that for an ideal gas $\rho_G T_G$ is constant assuming constant pressure in the sorber, the partial differential equations (B-1) and (B-2) with the boundary conditions (B-3a) and (B-3c) can be readily solved to give:

$$\begin{aligned} T_s(Z,t) &= 910\ e^{-\alpha Z - \beta t}\ I_o\ (2\sqrt{\alpha\beta Zt}) \\ &+ 675\ e^{-\beta t}\int_o^Z \alpha\ e^{-\alpha\xi}\ I_o\ (2\sqrt{\alpha\beta t\xi})\ d\xi \\ &+ 910\ e^{-\alpha Z}\int_o^t \beta e^{-\beta\eta}\ I_o\ (2\sqrt{\alpha\beta Z\eta})\ d\eta \qquad \text{(B-4)} \end{aligned}$$

where

$$\alpha = \frac{(1-\varepsilon)h}{s_G G} \qquad \text{(B-5a)}$$

$$\beta = \frac{h}{s_s\rho_s} \qquad \text{(B-5b)}$$

and I_o is the modified Bessel function of the first kind of order zero.

With the requirement that the temperature of the paper at the end of the sorber (Z=500) has to reach 400°F (860°R) for thermal desorption of SO_2, the batch time for the desorption mode is computed to be of the order of eight to nine hours and is approximately given by:

$$t \approx \frac{\alpha}{\beta} \times 500 = \frac{500(1-\varepsilon)s_s\rho_s}{s_G G} \qquad \text{(B-6)}$$

which in effect will make the regeneration mode batch time at least ten times longer than the sorption mode batch time. Furthermore, because of the long desorption batch time, the inner part of almost all the paper will reach 450°F by heat conduction before the surface of the paper near the effluent end of the sorber will be heated up. Since experimental data indicate that sorption of SO_2 on the paper is apparently a surface phenomenon, heating the bulk of the paper to above 400°F to desorb the SO_2 at a great expense of energy (which can be only partially recovered by cooling the bed with air entering the air preheater) is both unnecessary and time consuming. In addition, fairly large sorbent particles must be used to keep the pressure drop down, thus reducing the available surface area per unit volume of sorber for SO_2 sorption. The above argument would apply to all four cases considered and therefore the fixed bed design for sorption and desorption of SO_2 on paper does not appear to be an economical mode of operation for these applications.

APPENDIX C

COMPUTER PROGRAM USED IN EXPERIMENTAL DATA REDUCTION

```
C     FIXED BED SØRPTIØN CØMPUTER MØDEL
      DIMENSIØN X(1002,2),Y(1002,2)
      TYPE 5
    5 FØRMAT (//$INPUT - CØLUMN AREA, LENGTH, PRESSURE, TEMP,$,
     1/,8X,$GAS FLØW, SØ2 PER CENT, FINAL CØNC., SAT. PAPER,$,
     2/,8X,$PAPER DENSITY, VØID FRAC., KGA, H$//)
   10 ACCEPT 15, AREA,ZFINAL,P,TEMP,FSC,SØ2PC,YFINAL,QSAT,DEN,E,XKGA,H
   15 FØRMAT (4E12.6)
      CØ = SØ2PC * P/(10.73 * (TEMP + 460.))
      Q = QSAT/64.
      G = FSC * 14.7 * (TEMP + 460.)/(P * 520. * AREA)
      SFINAL = E*ZFINAL/G
   20 TYPE 21, SFINAL
   21 FØRMAT(///E12.6,/,$INPUT - DISTANCE INCREMENT, IFLAG, TIME-
     1 INCREMENTS,/)
      ACCEPT 25, IS,IFLAG,MT
   25 FØRMAT (3I4)
      AH = SFINAL/IS
      AK = 1./MT
      CØNY = (CØ * XKGA)/(DEN * Q)
      CØNX = (XKGA * H)/DEN
      CØNST = (XKGA * H * Q)/(E * CØ)
      TYPE 30
   30 FØRMAT (/////5X,$Y$,14X,$X$,27X,$TIME$,/,3X,$CG/CØ$,9X,
     1$CP/QSAT$,25X,$MIN$,//)
      IT = 1
      IS=IS+1
      THETA = 0.
      YT=0.
      YAVE = 0.
      DØ 100 N=1,IS
  100 X(N,1) = 0.
      Y(1,1) = 1.
      DØ 150 N=2,IS
  150 Y(N,1) = 0.
  200 S=0.
      Y(1,2) = 1.
      X1 = X(1,1)
      DX1 = CØNY * Y(1,1) - CØNX * X(1,1)
      DX=DX1
  202 X(1,2) = X(1,1) + DX * AK
      IF((X(1,2)-X1) - 1.E-2)204,204,203
  203 DX2 = CØNY * Y(1,2) - CØNX * X(1,2)
      DX = 0.5 * (DX1 + DX2)
      X1 = X(1,2)
      GØ TØ 202
  204 IF(X(1,2)-1.)225,205,205
  205 X(1,2)=1.
      Y(1,2)=1.
  225 DØ 280 M=2,IS
      X1 = X(M,1)
      Y1 = Y(M-1,2)
      DX1 = CØNY * Y(M,1) - CØNX * X(M,1)
      DY1 = -(XKGA/E * Y(M-1,2) - CØNST * X(M-1,2))
      DX=DX1
      DY=DY1
```

```
230 X(M,2) = X(M,1) + DX * AK
    Y(M,2) = Y(M-1,2) + DY * AH
    IF((X(M,2) - X1) - 1.E-2)235,235,240
235 IF((Y1 - Y(M,2)) - 1.E-2)245,245,240
240 DX2 = CONY * Y(M,2) - CONX * X(M,2)
    DY2 = -(XKGA/E * Y(M,2) - CONST * X(M,2))
    DX = 0.5 * (DX1 + DX2)
    DY = 0.5 * (DY1 + DY2)
    X1 = X(M,2)
    Y1 = Y(M,2)
    GO TO 230
245 IF(X(M,2) - 1.)255,250,250
250 X(M,2) = 1.
    Y(M,2) = Y(M-1,2)
255 S=S+AH
275 FORMAT (/3(1PE12.6,3X))
280 CONTINUE
    THETA = THETA + AK
    YT = YT + (Y(IS,2) + Y(IS,1)) * AK/2.
    YAVE = YT/THETA
296 IF(IT-MT/60)320,300,300
300 T = THETA * 60.
    TYPE 310, Y(IS,2),X(IS,2),T,YAVE
310 FORMAT (/1PE12.6,3X,1PE12.6,18X,1PE12.6,2X,1PE10.4//)
    IT = 0
320 IF(YAVE - YFINAL)330,400,400
330 DO 340 J=1,IS
    X(J,1) = X(J,2)
340 Y(J,1)=Y(J,2)
    IT = IT+1
    GO TO 200
400 T = (THETA - AK) * 60.
    TYPE 310, Y(IS,1),X(IS,1),T
    IF(IFLAG)598,425,410
410 ZH=0.
    SH=0.
    TYPE 415
415 FORMAT (/////5X,$Y$,14X,$X$,11X,$DISTANCE$,8X,$TIME$,/,3X,$CG/CO$
   1,9X,$CF/6SAT$,10X,$FEET$,12X,$MIN$,/)
    TYPE 416,T
416 FORMAT(45X,1PE12.6)
    DO 420 IA=1,IS,10
    TYPE 275, Y(IA,1),X(IA,1),ZH
    SH = SH + (AH * 10.)
420 ZH = SH * G/E
425 AZ = ZFINAL/IS
    TSO2 = 0.
    X(IS+1,1)=0.
    JS=(IS+1)/2
    JS=2*JS
    DO 510 KA=3,JS,2
510 TSO2 = TSO2 + (X(KA,1) + 4.* X(KA-1,1) + X(KA-2,1)) * AZ/3.
    TSO2 = TSO2 * Q * DEN * AREA
    TSO2LB = TSO2 * 64.
    VOL = AREA * ZFINAL
    PAPER = DEN * VOL
    TYPE 520, VØL,PAPER,T,TSØ2,TSØ2LB
520 FØRMAT(//////$VØL SØRBER - FT3$,8X,1PE12.6,/,$LBS PAPER
   1$,15X,1PE12.6,/,$BATCH TIME - MINS$,7X,1PE12.6,/,$SØ2 SØRBED
   2 - MØLS$,6X,1PE12.6,/,$SØ2 SØRBED - LBS$,7X,1PE12.6,////)
    GØ TØ 600
598 ACCEPT 599,XKGA
599 FØRMAT (E12.6)
    GØ TØ 20
600 TYPE 700
700 FØRMAT ($ PRØGRAM ENDS$)
    END
```